



# Overview on green synthesis of metallic nanoparticles

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## Abstract

Nanotechnology provides an advance way to solve the modern problems in modern world. The newly evolving technologies, more sustainable products and processes help us to lead a more eco friendly life. As researchers realized that a substance's physico—chemical properties like chemical reactivity, electrical conductivity, diffusivity, melting point, optical and mechanical properties were affected by its size, the importance of these materials became clear. Metal nanoparticles that are produced by green routes are non toxic in nature, no harmful by products are produced during the synthesis process, also this route gives a higher yield of nanoparticles as compared to other conventional methods. The varied phytochemistry of different biological extracts contains diverse chemical components that affects the nanoparticles and enhance their chemical or physical properties. This review so far discusses the green synthesis of metallic nanoparticles, their properties, various possible reducing sources, reduction mechanisms of different phytochemicals and how they are involved in the reduction process of metal ions, various examples of metal nanoparticle synthesis, their safety and toxicity concerns, how these green synthesized nanoparticles could be used in various fields, how biodiversity affects the green synthesis and also the sustainability impact of green synthesis over the environment, making this review unique.

**Keywords** Green synthesis · Phytochemistry · Metallic nanoparticles · Synthesis processes · Reduction mechanisms

## Introduction

Nanotechnology has progressed a lot in today's world therefore the synthesis of nanoparticles (NPs) has become so important now days as they are being employed in almost every sector. Though there are various different methods and approaches available in literature for synthesis of different nanoparticles, Green route /synthesis provides a rapid way for the synthesis of nanoparticles, using natural constituents with substantial reducing properties and excluding the use of obnoxious chemicals (Hussain et al. 2016). Nevertheless, for biomedical implementations where quality, safety, stability and sustainability of NPs is of serious importance, biogenic reduction of metal precursors to develop subsequent NPs is eco-friendly, less costly, free of chemical pollutants. Biogenic reduction/ Green synthesis is a " Bottom Up " method equivalent to chemical method where a reducing component is substituted by a green extract with intrinsic stabilizing,

finishing growth and capping abilities (Hussain et al. 2016). The usual properties of a particle changes as a result of particle size at the nanoscale (Bai and Liu 2013) ( $1\text{ nm} = 10^{-9}\text{ m}$ ), so the characteristics of a typical substance, such as conductivity, strength, color, etc., will vary greatly between the nanoscale and the macro scale.

The application of nanomaterials and nanoparticles is widespread and it is used in various sectors such as bio-medical sciences, mechanics, optics, electronics, chemical engineering, drug-gene delivery and in a lot of other sectors (Irvani 2011). The biological applications involves bactericidal, fungicidal, anti viral, anti inflammatory, anticarcinoma, antihyperglycemic and anti oxidant properties while the non biological applications may involve properties like photocatalysis and reduction properties (Patil and Kumbhar 2020). It has almost become a part of our daily lives. New techniques and novel procedures for the synthesis of nanomaterials such as carbon nanotubes (CNTs), metal nanoparticles, graphene and other nanocomposites have been the most talked about area in the field of nanoscience and technology in the last 10–12 years (Ahmad et al. 2010). The top down and the bottom up approaches have been the basic

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fundamental principles of synthesis of the nanomaterials (Fig. 1).

The “top down” approach involves starting from the larger structures and breaking it down to smaller ones till the nano scale is reached. This is usually done by etching or cutting techniques. The “bottom up” approach involves starting with the basic building materials, such as small atoms and molecules and assembling them until the required structure is formed (Ahmad et al. 2010). In these methods of synthesis, chemical reduction is one of the most common ways to synthesize metal nanoparticles of elements like silver, gold, etc. In the process, a lot of inorganic and organic reducing agents are used viz., sodium citrate, Tollen’s reagent, ascorbate, DMF and others along with critical physical property conditions. Besides these, several toxic capping agents are also used for the purpose of size stabilization. Li Yan et al. reported production of rod like  $\text{Mg}(\text{OH})_2$  nanoparticles from the hydrolysis of heptahydrate magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) in aqueous solution of ammonium hydroxide under hydrothermal condition (Yan et al. 2002).

Different morphological structures like rod, needle, lamella or tube, of  $\text{Mg}(\text{OH})_2$  were synthesized hydrothermally by the implication of various precursors of Mg powder,  $\text{MgSO}_4$ , and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were reported by Yi Ding et al. (Ding et al. 2001). Though these methods can produce a substantial number of nanoparticles in a short time span,

the main drawback is the hazardous nature and the toxicity associated with them. For example, Jihye Jang synthesized Si-embedded silicon oxycarbide using Si nanopowder, Silicone oil, anhydrous ethyl alcohol and cetrimonium bromide (CTAB) for surface modification of Si nanoparticles consisting of pyrolysis process at  $900\text{ }^\circ\text{C}$  (Jang et al. 2020). Sol gel synthesis of anatase titanium dioxide ( $\text{TiO}_2$ ) nanoparticles doped with copper using titanium (IV) isopropoxide and glacial acetic acid with aqueous solution of sodium dodecyl sulfate as capping factor, was detailed by Hemraj M. Yadava et al. (Yadav et al. 2014). The by-products produced by these processes are non-eco-friendly in nature. To solve these problems, green synthesis methods were thought of which does not make use of toxic chemicals for the biosynthesis of metal nanoparticles. Green synthesis, currently, is a vital branch of nanotechnology, which uses biologically derived entities like plants, plant parts, microorganisms or even biomass from plants for the synthesis of nanoparticles. This can be a potent alternative to the chemical and physical methods already being used. Some basic principles of green synthesis includes.

- Prevention/minimization of waste
- Less hazardous chemical synthesis
- Safer solvents and auxiliaries
- Reduction of derivatives/pollution

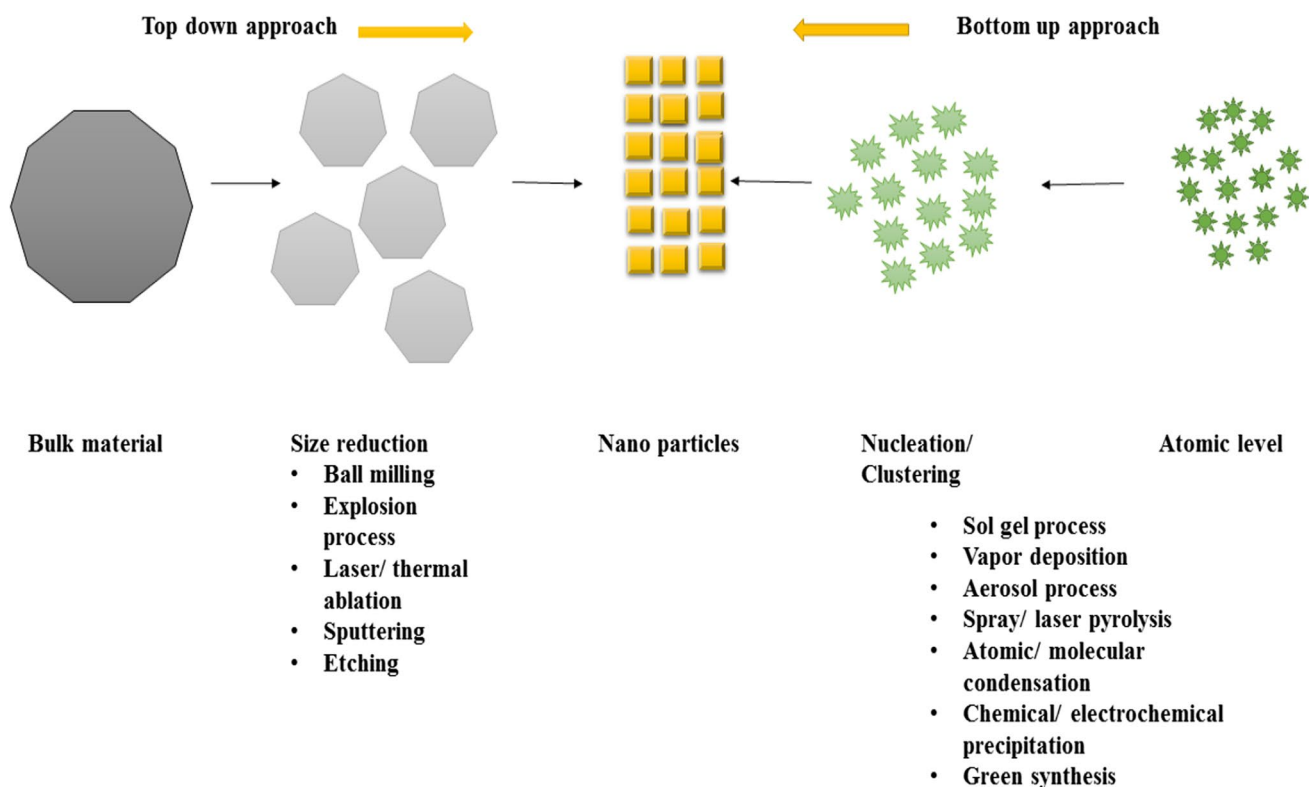


Fig. 1 Schematic diagram of the two approaches

- Design for energy efficiency (Ahmad et al. 2010)

## Production of metal nanoparticles by plants functioning as bioreactors

The use of different green (natural) parts like leaves, flowers, seeds, etc. for the production of metal or metal oxide nanoparticles is a simpler and easier approach as compared to microorganisms mediated synthesis process. The products formed are together known as biogenic nanoparticles (Ahmad et al. 2010). The potentiality of the botanicals to reduce metallic ions (be it in the interior or the exterior surface) has been a known phenomenon. Making use of this, plants have been used for phytomining (extracting precious land metals) of various priceless metals, which would otherwise be economically unjustifiable to mine. Good reducing and hyper accumulating abilities are the properties which are used for this purpose. Smelting and sintering methods are used for harvesting the metal elements and then they are recovered. One of the fascinating aspects of this process is that the deposition of the metal elements takes place in the form of nanoparticles (Makarov et al. 2014). Copper nanoparticles of size 2 nm were found in yellow iris (*Iris pseudacorus*) which were semi spherical (Manceau et al. 2008). In addition, *M.sativa* was found to contain gold icosahedra of 4 nm size (Gardea-Torresdey et al. 2002). There are several other examples where deposition of nanoparticles was found in various plant parts.

The presence of various effective phytochemicals in different plant extracts like leaves, stems, roots, flowers and seeds have been the reason for their ability to function as reducing agent and stabilizing agent. Various phytochemicals like ketones, terpenoids, aldehydes, phenols, carboxylic acids, flavonoids, etc., help to reduce the metal ions into metal nanoparticles (Singh et al. 2018). When it comes to using whole plants for the synthesis of metal nanoparticles it comes with certain restrictions and limitations. This arises especially when application in industries is taken into consideration (Gardea-Torresdey et al. 2002). Depending on the differences in the content of metal ions in the various tissues in the plant, the localization of the nanoparticles is determined, which further regulates the size and shape of the nanoparticles. New nucleation events and metal deposition around the formed nanoparticles are determined by the above factors (Gardea-Torresdey et al. 2002). When whole plants are used to synthesize nanoparticles one of the major issues is that fine-tuned sizes and forms, as well as nanoparticle quality, are very difficult to acquire. The non-homogeneous nature of the nanoparticles' size, morphology, and purity may preclude their use in applications that require nanoparticles of a particular

shape, size, and consistency (Rai and Yadav 2013)(Amini 2019). In addition, the processes of extraction, isolation and purification from the whole plant are not very easy and it also comes with low recovery. Comparing the in vitro and in vivo metal nanoparticle synthesis process where plants are considered as a system, the in vitro processes where plant extracts are used directly which also provides a considerable command over structural morphology of nanoparticles. This can be achieved by changing the pH of the solution, the reaction temperature, etc. This process is faster because it does not involve the delay required for the uptake and diffusion of the metal ions through the plant. It proceeds almost instantaneously and comes with easy purification. This approach has been shown by using the extract of various plant parts along with the salts of various metals like copper, magnesium, gold, silver, iron and others (Ghosh et al. 2012; Khan et al. 2013; Rai and Yadav 2013).

## Different plant parts involved in metal or metal oxide nano structure synthesis

Different structures can be achieved for metallic nanoparticles using various green parts like leaves, stems, seeds, fruits and roots via green route of synthesis (Fig. 2).



Fig. 2 Different parts of plants that can be used for Green synthesis

## Stem

Silver nanoparticles were synthesized from the methanolic extract of *Callicarpamingayi*. Aldehyde group which is present in substantial amounts in the plant extract was found to be responsible for the reduction of  $\text{Ag}^+$  ions to Ag nanoparticles (Yew et al. 2016). In another study, phyto reduction of silver ions to silver nanoparticles was possible when the stem extract of *C.aromaticus* was used (Vanaja et al. 2013). The stem part of the plant extract has been found to contain certain important functional groups like amines, carboxyl and phenolic compounds which are responsible for the reduction of silver ions. These biosynthesized silver nanoparticles are found to act as good antibacterial agents. Gulwaiz Akhter et al. reported the synthesis of copper nanoparticles using the stem extract of Holoparasitic plant (*Orobanche aegyptiaca*) and confirmed antimicrobial activity of the as synthesized Cu NPs against *E. coli* & *S. aureus* along with nematicidal properties against *Meloidogyne incognita* (Akhter et al. 2020).

## Fruit

Phytochemistry of fruit extract consists of anthocyanins, flavonoids, oxalic acids, sugars and other phenolic compounds with antioxidant and reducing properties (Rostamizadeh et al. 2020). Elham Rostamizadeh et al. 2020 reported the synthesis of  $\text{Fe}_2\text{O}_3$  nanoparticles from the fruit extracts of Cornelian cherry and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as metal precursor. Later these iron oxide nanoparticles were used for enhancing the growth of barley seedlings (Rostamizadeh et al. 2020). Silver nanoparticles were synthesized by the combination of fruit extracts of *Tribulusterrestris* and solutions of silver nitrate in varying molar concentrations. These were eco-friendly along with particular structural features. The active phytochemistry of the extracts i.e. the constituents of the extracts are suggested to be responsible for the reduction reaction (Gopinath et al. 2012). Synthesis of palladium nanoparticles was also performed in a similar way by using polyphenol from grapes. They were found to be effective against certain bacterial diseases (Amarnath et al. 2012). Au and Ag nanoparticles were also synthesized by the reduction and stabilization effect of flower extracts of *Lycium Chinese* fruit and gold (III) chloride trihydrate and silver nitrate solutions as metal precursors. These nanoparticles showed inhibitory activity against bacterial infections of *Staphylococcus aureus* and *Escherichia coli* (Chokkalingam et al. 2019).

## Seed

Wide varieties of seeds and their aqueous extracts have been used for nanoparticle synthesis in various studies. Harekrishna Bar et al. 2009 synthesized silver

nanoparticles using aqueous seed extracts from *Jatropha curcas* plant and aqueous solution of silver nitrate as metal precursor. *J. curcas* is a potential biodiesel crop containing high percentage of crude fat and proteins along with olic acid, linolenic acid, palmitic acid and stearic acid. The functional groups of these biomolecules have the potential of reduction of metal ions and capping properties in the growth step of the synthesis process. (Bar et al. 2009) High quantities of flavonoids and other bioactive products like saponin, lignin and vitamins are present in the fenugreek seed extract. This seed extract functions both as a reducing agent as well as a surfactant. The carboxylic group and other functional groups act as surfactants of the gold nanoparticles whereas, the flavonoids function as electrostatic stabilizers of the gold nanoparticles (Mittal et al. 2013). The aqueous extract of *Macrotylomauniflorum* was found to enhance the rate of reduction of the silver ions, the reason of which was thought to be the presence of caffeic acid in the extract (Kuppusamy et al. 2016). In another example of silver nanoparticles synthesis, seed extracts of *Pimpinella anisum* were used with aqueous solution of silver nitrate and the resulting nanoparticles showed high cytotoxic properties against cancerous cells by the induction of apoptosis. (Devanesan et al. 2017).

## Leaves

Extensive study of the use of plant leaves' extract as a mediator for the synthesis of nanoparticles has been done. Stable palladium nanoparticles were synthesized by using 1 mM of  $\text{PdCl}_2$  and *Piper betle* in the ratio of 10:1. They were found to inhibit the growth of the fungus *Aspergillus niger* (Mallikarjuna et al. 2013). An important bioactive material was said to be present in the leaves of *P.nigrum* which is involved in the nanoparticle synthesis by eco-friendly methods. The leaves of *Artemisia nilagirica* extract was used for the synthesis of Ag nanoparticles which was seen to show substantial antibacterial activity (Vijayakumar et al. 2013). C.P. Devatha et al. 2016 reported the synthesis of iron nanoparticles from different leaves extracts of *Mangifera indica*, *Murraya Koenigii*, *Azadiracta indica* and *Magnolia champaca* (which are available plentiful in India) with Ferrous sulfate heptahydrate. All these extracts are rich in saponins, phenols and tannins which have different reducing properties and thus initiate the reduction reaction of metal ions. Further these iron nanoparticles were used for domestic waste water treatment out of which nanoparticles synthesized from *A. indica* showed high percentage of removal of phosphates, ammonia and nitrogen up to a great extent and reduction in chemical oxygen demand (COD) of the domestic waste water sample as compared to nanoparticles produced from other leaves extracts (Devatha et al. 2016).



## Flowers

Rose petals have been used in an eco-friendly procedure to produce gold nanoparticles. The extract mixture contains plentiful sugars and proteins, which are the primary contributors for the reduction of tetrachloroaurate salts into gold nanoparticles (Noruzi et al. 2011). Gopalu karunakaran et al. 2017 used *Hydrangea paniculata* flower extract for the synthesis of Mg nanoparticles and Ag nanoparticles. The major components of the extracts were found to be terpenoids, steroid, saponins, alkaloids, quinone, glycosides and flavonoid which played a key role in the reduction of metal precursor and stabilization of the nanoparticles. Both of the as synthesized nanoparticles showed antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* (Karunakaran et al. 2017). Another example of flower extracts involves the synthesis of zinc oxide nanoparticles from the flower extracts of *Nyctanthes* with zinc acetate dihydrate. *Nyctanthes* is a medicinal plant and used in *Ayurveda* as it possesses anti-helminthic, antimicrobial, antiviral, anti-leishmania, anti-allergic, anti-diabetic and anti-cancerous properties along with sedative and laxative agent. Even the concentrations of precursor and reducing agents were optimized in this study to obtain the desired size of zinc nanoparticles (Jamdagni et al. 2018). In a similar manner, flowers of diverse groups of *Catharanthus roseus* and *Clitoria ternatea* were used for metal nanoparticle synthesis of desired shapes and sizes. These nanoparticles have been very effective in controlling the harmful pathogen bacteria. *Nyctanthes arbor-tristis* flowers, which have potential medical uses, were used to synthesize gold nanoparticles via green synthesis approach (Das et al. 2011).

## Other biological components for green synthesis

As discussed, there are several methods for the synthesis of metal nanoparticles which involve high radiation, highly toxic materials being used as reductants and stabilizing agents and those which are non-biodegradable. These can cause enormous amounts of harm to both the terrestrial as well as marine life. On the other hand, green synthetic methods are eco-friendly as well as cost-efficient. Below are mentioned some components of green synthesis, other than the plant or plant parts, which can and are being used for the development of various metal nanoparticles (Dahoumane et al. 2016).

### Bacteria

A number of bacterial species have been used in infomercial biotechnological processes, such as genetic engineering,

bioremediation and bioleaching. Bacteria have the unusual potential to reduce metallic ions and hence play a central role in the preparation of nanoparticles. Prokaryotic bacteria and actinomycetes are the most commonly used among the various bacterial species available for the synthesis purpose regarding nanoparticles (Mitra et al. 2018). The main advantage of using bacteria for production of nanoparticles is the relative ease with which the bacteria can be manipulated to suit our requirement (Thakkar et al. 2010). The bio reduction of silver ions to nano particles has been commonly done by many bacterial strains. Some of these involve *E. coli*, *L. casei*, *B. cereus*, *Aeromonas* sp. SH10 *Phaeocystis antarctica*, *Pseudomonas proteolitica*, *B. amyloliquefaciens*, *Bacillus indicus*, *Enterobacter cloacae*, *Geobacter* species, *Arthrobacter gangotriensis*, *Shewanella oneidensis* and *Corynebacterium* species. Similarly, numerous bacterial species have been utilized for gold nanoparticles synthesis some of which are, *Bacillus megaterium* D01, *Desulfovibrio desulfuricans*, *E. coli* DH5a, *Shewanella alga*, *Rhodospseudomonas capsulata*, and *Plectonemaboryanum* UTEX 485 (Kaur et al. 2019). Different bacteria including *E. coli*, fermentative bacteria and dissimilatory metal reducing bacteria has been studied for biological metal precipitation. The main principle of these bacteria for reduction of metal ions is hydrogenation. A different part of bacteria like cytoplasm, periplasm and cytoplasmic membrane contains different hydrogenase enzymes, these parts acts as the initiation points for the reduction reaction of metal ions. In case of *Desulfovibrio*, when the nanoparticles are formed intracellular i.e. in periplasm of outer plasma membrane, then the synthesized nanoparticles are naturally stabilized and capped due to the polymers that are naturally present in that area/ part. Also the native polymers controls the growth and inhibits the aggregation of the nanoparticles (Yates et al. 2013) while in case of other bacteria, reductases plays a key role in the reduction reaction (Das et al. 2012).

### Fungi

Monodispersed nanoparticles with complex morphologies can be developed very efficiently by biosynthetic pathway from metals and metal oxides mediated by fungi. They are effective biological agents metal nanoparticles production, as a variety of intracellular enzymes is found in them and as a result, In contrast to bacteria, fungi can synthesize greater quantities of nanoparticles. A number of proteins, enzymes and reducing components are present on the cell surfaces of the fungi giving them a major advantage over other organisms (Mohanpuria et al. 2008; Narayanan and Sakthivel 2011; Wang et al. 2014a). Enzymatic reduction by the enzyme reductase inside the fungal cell or in the cell wall is thought to be the probable mechanism for synthesis of nanoparticles. Several metals

like gold, zinc oxide and silver have been synthesized by different fungal species (Kaur et al. 2019). Silica nanoparticles were synthesized during the growth of *Agaricus bisporus* humus fungi with  $\text{Na}_2\text{SiO}_3$  and the range was found to be in 30–100 nm (Vetchinkina et al. 2019). Sujoy K. Das et al. 2012 reported the intracellular biosynthesis of gold nanoparticles from *Rhizopus orizae* fungi. The mycelia of the fungi was allowed to grow in presence of Au(III) ions and it resulted in the intracellular metabolism of gold nanoparticles which even affected the cellular growth and protein expressions of the *R. orizae* (Das et al. 2012). According to a study, it has been suggested that nitrate reductase and  $\alpha$ -NADPH-dependent reductases are mainly responsible candidates for the synthesis of nanoparticles. Also on the condition of extracellular synthesis of nanoparticles, they are stabilized by a set of different proteins and enzymes having high molecular weight that are secreted by the fungi itself (Pramila Khandel 2018). In another study, Qianwei Li et al. studied the extracellular synthesis of nanoscale copper carbonate due to the effect of extracellular enzymes secreted by ureolytic fungi like *Neurospora crassa*, *Pestalotiopsis species* and *Myrothecium gramineum* (Li and Gadd 2017).

## Yeast

They are the single celled microorganisms which are found in the eukaryotic cells. Different research groups have documented successful synthesis of nanoparticles via yeast. *Saccharomyces cerevisiae* broth and silver resistant yeast strain biosynthesis of gold and silver nanoparticles has been recorded. For the synthesis of different nanoparticles, numerous species of yeasts (total of 1500 have been found) have been used (Yurkov et al. 2011). Hollow yeast cellular fragments were used for the sheet by sheet synthesis of DNA nanoparticles and their targeted delivery to phagocytic cells in one of the research papers. (Soto and Ostroff 2008). Guanglei Ma et al. reported the synthesis of vinyl polymer nanoparticles inside hierarchical yeast cell particles. These yeast cells have the ability to carry and release the nanoparticles like Trojan particles according to the situation (Ma et al. 2016).

## Role of plant metabolites in the formation of the metal nanoparticles

As already mentioned, various plant metabolites such as flavonoids, terpenoids, sugars, polyphenols, alkaloids and proteins play a very important role in the formation of metal nanoparticles.

## Terpenoids

Terpenoids are morphologically the most varied natural product and also called as isoprenoids. The different types of terpenoids are Hemiterpinoids, Monoterpinoids, Iridoids, Sesquiterpenoids, Diterpenoids, Sesterterpenoids, Triterpenoids, Tetraterpenoids and Polyterpenoids. Monoterpenoids is the key component in essential oils and is responsible for the aromatic smell in various plants like rose, mint, pine, Cyprus and many more. Carotenoid is an example of tetraterpenoid and act as an accessory and coloring pigment in different plants. Also they possesses antibacterial activity against various Gram positive and gram negative bacteria (Ludwiczuk et al. 2017). Fourier-transform infrared spectroscopy (FTIR) of the nanoparticles synthesized with the help of plant extracts was performed and it showed that one of the compounds which were associated with the synthesis of nanoparticles was terpenoids. They are known to display strong antioxidant activity. They are basically synthesized from 5 carbon isoprene units and they comprise of diverse organic polymers. In the reaction involving conversion of silver ions into silver nanoparticles making use of geranium leaves extract, terpenoids were thought to play a key role. Further, the main terpenoid of cinnamon extract, eugenol, was the key component in the bio reduction of  $\text{HAuCl}_4$  and  $\text{AgNO}_3$  into their corresponding metal nanoparticles. Based on FTIR study, it was deduced that the dissociation of a proton of the eugenol—OH group leads to the formation of structures (resonant), which are capable of further oxidation. This method is accompanied by the active reduction of metal ions and the formation of nanoparticles, thereafter (Singh et al. 2010)(Goyal et al. 2019).

## Flavonoids

Beside the terpenoids, the flavonoids are also one of the essential components in the synthesis of nanoparticles by green synthesis method. They are phenolic compounds and are present in various vascular plants; contribute as pigments for attracting insects and other pollinating agents due to their attractive scarlet, blue or orange color in leaves, flowers and fruits. They also catalyses the light phase in photosynthesis and absorbs the UV rays resulting in the protection of plant (Pietta 2000). Numerous classes of flavonoids including chalcones, isoflavonoids, anthocyanins, flavonols and flavones have the capacity to reduce metal ions and they can also act as active chelating agents. The release of a reactive hydrogen atom upon transformation from the enol form to the keto form (tautomers) is considered to be the logic for the reduction of metallic ions into nanoparticles. Like for example, in *Ocimum basilicum* extract, two of the flavonoids known are luteolin and rosmarinic acid, and their transition from the enol type to the keto type serves a crucial

role in transforming  $\text{Ag}^+$  ions to Ag nanoparticles. (Iqbal et al. 2019). In addition, the reduction of the  $\text{Au}^{3+}$  ion due to flavonoids mostly involves the modification of ketones to carboxylic acid. The flavonoids' chelating activity is attributed to their carbonyl functional groups or  $\pi$  electrons. Quercetin is one of the flavonoids with very strong chelating action because it can chelate at three positions involving the carbonyls and the hydroxyls. Due to the presence of such mechanisms, on the exterior of the fledgling nanoparticles, flavonoids can be adsorbed, most likely suggesting that they are involved in the activation phases. and further aggregation along with the bio reduction stage (Makarov et al. 2014).

## Sugars

Many sugars like fructose and glucose which are found in the plant extracts are also involved in nanoparticle formation. Silver and gold nanoparticles which are fructose mediated are found to be mono dispersed in nature (Zayed et al. 2012). In another study, synthesis of silver nanoparticles was reported from honey carbohydrates (González Fa et al. 2017). Monosaccharides which contain a keto group (e.g., fructose) have to convert from its keto form to aldehyde to function as an antioxidant. In the case of disaccharides and polysaccharides, the ability of its monosaccharide components to adopt an open chain form to provide access to an aldehyde group determines their reducing capability (Zayed et al. 2012).

## Proteins

Proteins are crucial in the development of anisotropic nanoparticles without the use of toxic surfactants. Proteins have been used even to create nanoparticles of various shapes and sizes. Protein corona is a post-synthesis alteration that uses proteins to modify the surface of nanoparticles (Chakraborty and Parak 2019). Amini et al. created gold nanorods and nanoparticles coated with CTAB and PEG to treat cancerous cells' hyperthermia, and discovered that the surface chemistry and morphology of the nanoparticles had a significant impact on the outcomes (Amini et al. 2018). When the FTIR analysis of nanoparticles was performed, embryonic nanoparticles were consistently found to be protein-associated (Zayed et al. 2012). Amino acids (lysine, cysteine, arginine and methionine) have also been found to be excellent in bonding with silver ions (Clem Gruen 1975). Proteins and carbohydrates are present in the plant extract which helps to reduce the metal ions (Iravani 2011). Proteins containing amino groups present in green extracts have also been found to be able to effectively participate in the synthesis of silver nanoparticles (Li et al. 2007). Literature also suggests that proteins such as Lysozyme produce spherical nanoparticles, while Bovine serum albumin (BSA) and catalase produce

anisotropic nanoplates. Proteins have a lot of versatility in terms of sequence of amino acids, size of the side chains, and shape of the overall structure, so they can be used as ligands. Each protein has a branch of amino acid residues with oxygen, nitrogen, and sulfur-bearing groups that can help to reduce and guide the structure of the nanoparticle by adsorbing on a particular location on the nanoparticle surface. (Chakraborty and Parak 2019).

## General mechanism of green synthesis

Framework of the formation of nanoparticles via botanical extracts is shown in Fig. 3.

Overall, there are three main steps in the mechanism of nanoparticle formation through plant extracts: (1): the activation stage in which metallic ions are reduced and the atoms of the metal begin to nucleate (2): growth phase where the metal atoms coalesce amongst each other to form larger particles (nanoparticles are directly formed by heterogeneous nucleation and growth and further ion reduction; this is known as Ostwald ripening); this leads to increased thermodynamic stability of the nanoparticles and (3): termination phase which determines the final shape of the nanoparticles. It depends on the length of the growth phase which type of nanoparticles will be formed; be it the nano prisms, the nano hexahedrons or the nanotubes or simply irregularly shaped nanoparticles (Makarov et al. 2014).

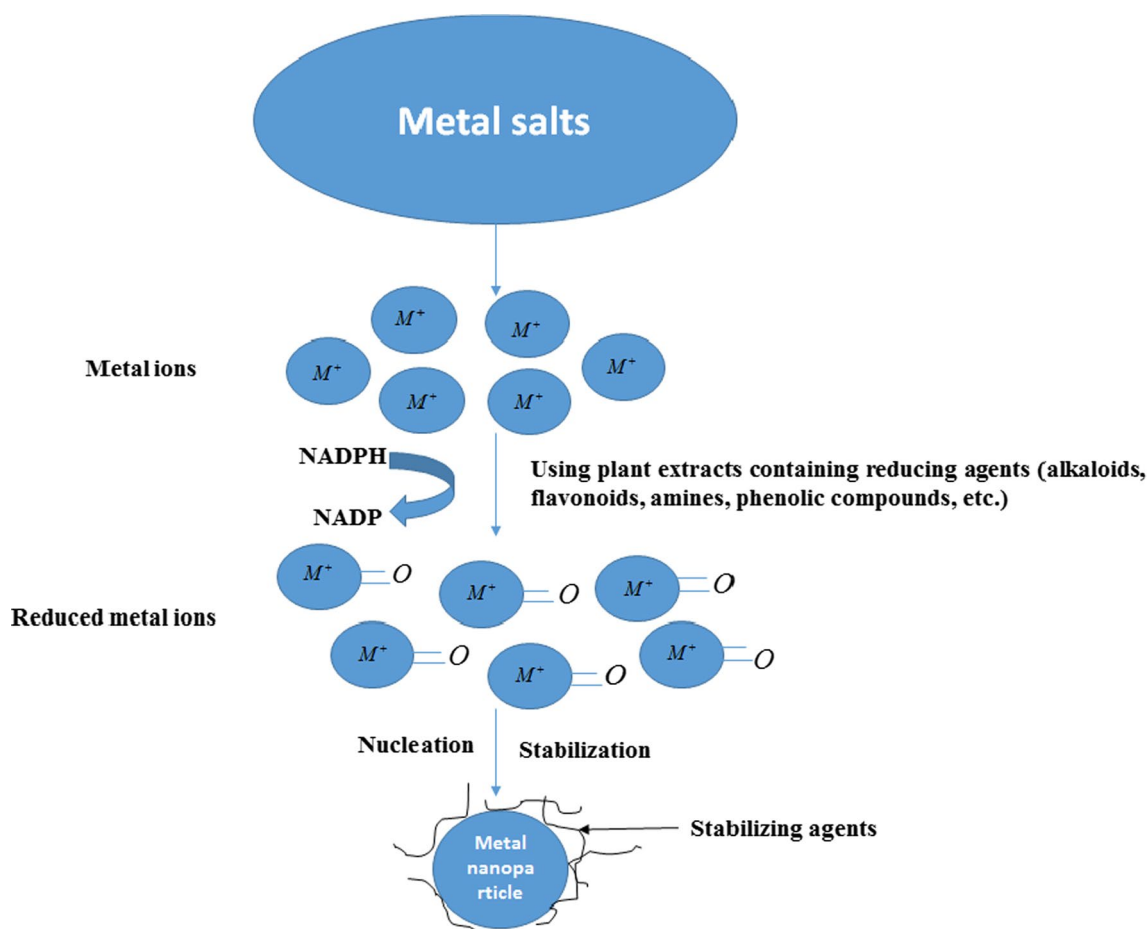
## Green synthesis of some metal/metal oxide nanoparticles

### Gold nanoparticle

Noble metal elements consisting of platinum (Pt), silver (Ag) and gold (Au) forms one of the most important classes of metal nanoparticles (Abdelghany et al. 2015). Among these metals, gold has been able to catch much of the attention due to its ability to interact with light by SPR (Surface Plasmon Resonance) (Wang et al. 2014a). Recent studies have shown that gold NPs have the potential to serve as building blocks for plasmonic devices and further, their use as bio molecular conjugates is also much talked about (Narasaiah and Mandal 2020). Some of the examples of synthesis of Au nanoparticles are summarized in the Table 1.

### Silver nanoparticle

Silver nanoparticles have been found to have certain attractive properties and because of it, they have gained much attention. Properties like high chemical stability and catalytic activity, good antimicrobial activities, high thermal and electrical conductivity and surface-enhanced



**Fig. 3** General mechanism for nanoparticle formation through green synthesis

Raman scattering have made Ag NPs materials of high demand (Jeyaraj et al. 2013). Different chemical and physical methods for the synthesis of Ag NPs with required size and shape and antibacterial properties have been demonstrated before. Some of the examples for the synthesis of Ag nanoparticles are summarized in the Table 2.

### Zinc oxide nanoparticle (ZnO)

Superconducting materials, catalysts, ceramic resistors and gas sensors are some of the prominent and important roles served by the ZnO nanoparticles. In addition, they are safe to use and also inexpensive. The US FDA has listed ZnO as GRAS (generally recognized as safe) metal oxide (Adams and Barbante 2013)(Agarwal et al. 2017). Some of the plant sources which have been used to synthesize ZnO nanoparticles are summarized in the Table 3. Further, some other metal/metal oxide nanoparticles which were synthesized from different plant sources are mentioned.

### Copper/Copper oxide nanoparticle

Copper/copper oxide nanoparticles find its main application in electronic devices, medical equipment, biosensors etc. due to its catalytic, mechanical, magnetic, electric and thermal properties. Also, they possess antibacterial and antifungal properties which make them useful in pharmaceuticals. They are useful in targeted drug delivery because of their non-toxicity and nanometer size. Some sources for the synthesis of copper/copper oxide nanoparticles are listed below in Table 4.

### Iron/Iron oxide nanoparticle

Green synthesis of iron/iron oxide nanoparticles is cost effective, nontoxic and eco-friendly. Fe nanoparticles possess multi-valent oxidation states and its characteristic structure at Nano scale plays a major role in catalysis, imaging, biosensors, gene delivery and targeted drug delivery. Magnetic and ferromagnetic properties of these NPs attract



**Table 1** Examples of gold nanoparticles synthesis

Material precursor	Reducing agent used	Amount of extract	Size of nanoparticle (nm)	Morphology	Properties	References
Gold (III) chloride trihydrate	<i>Agaricusbisporus</i>	Gold (III) chloride trihydrate (1 mm) solution was prepared by dissolving 0.392 g of its powder in 100 ml of DDW. Later 8–12 ml of this mixture were mixed with 1 ml of mushroom extract with different concentrations	25	Spherical	Antifungal activity	(Eskandari-Nojedehei et al. 2018)
$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	<i>Dalbergiacoromandeliana</i>	Ethanollic solution of dalspinin extracted from roots of Dalbergiacoromandeliana (1 mL) at a concentration of ( $1 \times 10^{-3}$ M) was slowly added to the fresh aqueous solution of (5 mL) $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ( $1.4 \times 10^{-3}$ M) continuous stirring for 10 min	10.5	Spherical	Catalytic activity (degradation of Congo red and Methyl orange.)	(Umamaheswari et al. 2018)
Chloroauric acid	<i>Croton Caudatus Geisel Leaf</i>	10 ml of the leaf extract was mixed with 90 ml of 1 mM chloroauric acid	20–50	Spherical	Antifungal and antimicrobial activity	(Vijaya Kumar et al. 2019)
Chloroauric acid	<i>Thymus vulgaris leaf</i>	Aqueous extract (10 ml) was added to the aqueous solution of (1 mM) $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ (100 ml)	10–30	Spherical	Antioxidant property	(Hemmati et al. 2020)
$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	<i>Hibiscus sabdariffa flower</i>	(10 ml) extract was added to aqueous 1 mM solution of $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$ (100 ml)	15–45	Spherical	Medicinal properties (chemotherapeutic drug for the treatment of acute myeloid leukaemia in the clinical trial)	(Tahvilian et al. 2019)
$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	<i>Cinnamon sticks</i>	Cinnamon solution was added to the 1 mM aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	13–20	Anisotropic (spherical, triangular, hexagonal)	Antibacterial activity	(Goyal et al. 2019)
Chloroauric acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ )	<i>Sodium borohydrate</i>	Fresh ice cold 25 ml 0.2 M $\text{NaBH}_4$ was added dropwise to aqueous solution of 0.5 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	2–3	Spherical	Thermal therapy	(Amini et al. 2018)

Table 1 (continued)

Material precursor	Reducing agent used	Amount of extract	Size of nanoparticle (nm)	Morphology	Properties	References
H <sub>2</sub> AuCl <sub>4</sub> ·3H <sub>2</sub> O	<i>Trisodiumcitrate</i>	1 ml of 140 mM trisodium-citrate solution was added to 100 ml of 0.25 mM aqueous solution of H <sub>2</sub> AuCl <sub>4</sub> ·3H <sub>2</sub> O	5–17.7	Spherical	Biosensors	(Fatemi et al. 2017)
Tetrachloroauric acid	<i>Trisodiumcitrate</i>	40 mM trisodium citrate solution (12.5 mL) was added rapidly to the boiling solution of Tetrachloroauric acid	16	Spherical, faceted	Biosensors	(Emami et al. 2015)
H <sub>2</sub> AuCl <sub>4</sub> ·3H <sub>2</sub> O	<i>Sodium borohydrate</i>	0.5 ml of fresh ice-cold sodium borohydrate (0.1 M) was added to mixture of 0.5 ml CTAB and H <sub>2</sub> AuCl <sub>4</sub> ·3H <sub>2</sub> O and stirred vigorously	6	Spherical	Drug delivery	(Zarchi et al. 2018)
H <sub>2</sub> AuCl <sub>4</sub>	<i>Sodium borohydrate</i>	To a 12 ml solution of 0.5 mM H <sub>2</sub> AuCl <sub>4</sub> and 0.5 ml, 10 mM sodium citrate, 0.5 ml of 10 mM solution of sodium borohydrate added rapidly and stirred vigorously	1–25	Spherical, faceted	Drug delivery	(Amini et al. 2013)
Chloroauric acid	<i>Marine brown algae</i>	5 ml of Aqueous extracts of the algae were added to 45 ml of 1 mM aqueous AuCl <sub>4</sub> solution	27–35	Spherical	Catalytic activity (reduction of Rhodamine B and Sulforhodamine 101 hydrate)	(Ramakrishna et al. 2016)
Chloroauric acid	<i>Stevia rebaudiana Bertoni</i>	stevia leaf extract is mixed rapidly with 0.1 mM AuCl <sub>4</sub> —solution in equal volume	5–20	Spherical	Biomedical and pharmaceutical	(Sadeghi et al. 2015a)
Chloroauric acid	<i>Olea europaeafruit extract and Acacia nilotica husk extract</i>	5 ml of centrifuged and pure extracts of both the fruit and husk was added to the aqueous solution of 1 mmol/mL H <sub>2</sub> AuCl <sub>4</sub>	45	Spherical	Antibacterial activity	(Awad et al. 2019)
Chloroauric acid	Leaf extracts of <i>Carica papaya</i> and <i>Catharanthus roseus</i>	1 mM of chloroauric acid was reduced separately using both leaf extracts in varying concentrations	15–28	Spherical, triangle, hexagonal	Antibacterial and anticancer activity	(Muthukumar et al. 2016)

**Table 2** Examples of silver nanoparticle synthesis

Material precursor	Reducing agent used	Amount of extract	Size of nanoparticle (nm)	Morphology	Properties	References
Silver nitrate	<i>Jatropha curcas</i>	20 ml of 3% latex solution in 20 ml of $5 \times 10^{-3}$ M aqueous silver nitrate solution	15–50	Crystalline	stability	(Bar et al. 2009)
Silver nitrate	<i>Argemone mexicana</i>	10 ml of extract was added to 90 ml of aqueous solution of 5 mM $\text{AgNO}_3$	25–50	cubic	Antimicrobial property	(Singh et al. 2010)
Silver nitrate	Carob leaf	5 ml of extract to 100 ml of $1 \times 10^{-3}$ M aqueous $\text{AgNO}_3$ solution	5–40	spherical	Antibacterial property	(Awwad et al. 2013)
Silver nitrate	<i>Azadirachta indica</i>	1, 2, 3, 4 and 5 mL of plant extract was added separately to 10 mL 1 mM $\text{AgNO}_3$ solution	34	Spherical to irregular	Antimicrobial property	(Ahmed et al. 2016)
Silver nitrate	<i>Nerualtazeylanica</i> leaf	10 ml leaf extract added to 90 mL of silver nitrate (1 mM) solution	20–50	Spherical	Catalytic activity (dye degradation), antimicrobial activity	(Vijayan et al. 2019)
Silver nitrate	<i>Andrographis paniculata</i> , <i>Phyllanthus niruri</i> , and <i>Tinospora cordifolia</i>	Respective plant extract were added to 1 mM aqueous solution of $\text{AgNO}_3$	70–95 70–150 50–70		Antiviral potential (against chikungunya virus)	(Sharma et al. 2019)
Silver nitrate	<i>Ficus benghalensis</i> leaf	25 ml of $\text{AgNO}_3$ solution mixed with 1 ml of leaf extract	5–60	Spherical	Antimicrobial activity	(Maniraj et al. 2019)
Silver nitrate	<i>Amorphophallus paeoniifolius</i> Leaf	Varying volumes of extract added to 0.1 mM 100 ml $\text{AgNO}_3$ solution	20–30	Spherical	Antibacterial activity	(Gomathi et al. 2019)
Silver nitrate	<i>Falcaria vulgaris</i> leaves	10 ml Extract added to 100 ml of a $1 \times 10^{-3}$ M aqueous solution of silver nitrate	40–45	spherical	Non- cytotoxicity, antioxidant, antibacterial, antifungal and cutaneous wound healing activities	(Tahvilian et al. 2019)
Silver nitrate	<i>Ocimum sanctum</i> leaf	10 ml of extract and 90 ml of silver nitrate ( $\text{AgNO}_3$ ) solution mixed to make the final concentration to $10^{-3}$ M	10–50	spherical	Antimicrobial activity (Nano engineered tissue paper coating)	(Jacob et al. 2019)
Silver nitrate	<i>Bacillus licheniformis</i> M09	sterile $\text{AgNO}_3$ (1 mM) added to the cell-free supernatant (1:1 v/v)	10–30	Spherical	Photo catalytic dye degradation, antibacterial activity, and cytotoxicity	(Momin et al. 2019)
Silver nitrate	<i>B. methylotrophicus</i> DC3	Centrifuged supernatant of the bacterial suspension was mixed with $\text{AgNO}_3$ solution at a 1 mM final concentration and incubated	10–30	Spherical	Antimicrobial activity	(Wang et al. 2016)
Silver nitrate	<i>Berberis vulgaris</i> leaf and root	100 ml of $\text{AgNO}_3$ solution with 0.5, 1, 3 and 10 molar concentrations were added to a 3, 5, 10, 15 and 30 mL of aqueous extract and heated	30–70	Spherical	Antibacterial activity	(Behravan et al. 2019)

Table 2 (continued)

Material precursor	Reducing agent used	Amount of extract	Size of nanoparticle (nm)	Morphology	Properties	References
Silver nitrate	<i>Pistacia atlantica</i>	1 mL of the extract was added to 10 mL of 1 mM silver nitrate ( $\text{AgNO}_3$ ) solution and kept on a orbital shaker at room temperature	27	Spherical	Antibacterial activity	(Sadeghi et al. 2015b)
Silver nitrate	<i>Hydroxyapatite</i> surface	100 mg Polydopamine coated Hydroxyapatite was dissolved in a 100 mL aqueous solution of silver nitrate and stirred for 24 h	14–15	Spherical	Catalytic activity (reduction of 4-nitrophenol)	(Das et al. 2018)

various applications in supercapacitors, lithium-ion batteries and electro catalysis. Some examples for the synthesis of Fe NPs are listed in Table 5.

### Palladium nanoparticle

Palladium nanoparticles among the noble metal nanoparticles possess high surface to volume ratio and high reactivity. Hence, they show both homogeneous and heterogeneous catalysis and are used in synthesis of various fine chemicals in preparative chemistry. These nanoparticles also show adsorption and reduction properties and can be used in water purification processes. Green synthesis provides a more efficient, nontoxic and eco-friendly way for the synthesis of palladium nanoparticles. Some of the methods that have been used for the synthesis of palladium nanoparticles are shown in Table 6.

### Titanium dioxide nanoparticle

Titanium dioxide nanoparticles show high photo catalytic activity, are chemically stable and have strong oxidizing power. They are thermally stable, possess excellent optical and dielectric properties and are bio compatible and nontoxic. Semiconductors, photovoltaic, lithium ion batteries, medicines, sensors, agro-food products, coating materials etc. are some areas of application of titanium oxide nanoparticles. Various toxic chemicals are eliminated by applying a green route of synthesis of nanoparticles. Few examples for the synthesis of  $\text{TiO}_2$  NPs are tabulated in Table 7.

## Applications of the biosynthesized nanoparticles

### In food industry

White colored food products like sauces, creams and confectionaries contains  $\text{TiO}_2$  nanoparticles up to some extent as it helps to maintain the white texture of sweet items and other non dairy products (Waghmode et al. 2019). The metallic nanoparticles are used as biosensors as due to the open scale processes there is a high chance of microbial contamination; and the work of the biosensors is to evaluate the quality of the products by detecting pathogens. Moreover, these biosensors, made of the nanoparticles, are of low cost (Kuppasamy et al. 2016). Silica nanoparticles are used in food packaging materials as they provide a barrier for the food coming in contact with moisture and other gases like oxygen which can ultimately spoil the food and reduce its shelf life (Asmathunisha and Kathiresan 2013). Zinc oxide is generally considered as safe as food additives by food and drug administrations, so nanoscale zinc oxide is used



**Table 3** Examples of zinc/zinc oxide nanoparticles synthesis

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Zinc gluconate hydrate ( $C_{12}H_{22}O_{14}Zn \cdot xH_2O$ )	<i>Carica Papaya</i> seed	100 mL of zinc gluconate hydrate (0.1 mol L <sup>-1</sup> ), 100 mL of seed extract and 100 mL of NaOH (0.4 mol L <sup>-1</sup> ) were added while stirring the mixture	Zinc oxide	4–8	Spherical	Electrochemical sensing (biosensors)	(Sharma et al. 2018a)
Zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ )	<i>Garcinia mangostana</i> fruit	50 ml extract was boiled at 70–80°C. Later, 4 g of zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ) was added slowly	Zinc oxide	21	Spherical	Photo catalytic activity (photo degradation of MG dye)	(Aminuzzaman et al. 2018)
Zinc sulphate ( $ZnSO_4$ )	<i>Tecomacastanifolia</i> leaf	10 ml of extract is added to 90 ml of 1 mM zinc sulphate solution	Zinc oxide	70–75	Spherical	Antibacterial, anti-oxidant, anticancer activities	(Sharmila et al. 2019)
Zinc nitrate hexahydrate	<i>Rhamnusvirgata</i>	6 g of salt zinc nitrate hexahydrate was added into 100 mL plant extract	Zinc oxide	20–30	Hexagonal	Antibacterial and antifungal activities	(Iqbal et al. 2019)
Zinc acetate	<i>Aloe socotrina</i> leaf	aqueous leaf extract of <i>A. socotrina</i> (10 mL) was added to 1 mM of aqueous zinc acetate	Zinc oxide	15–50	Spherical	Antibacterial activity	(Fahimmunisha et al. 2020)
Zinc nitrate	<i>Beta vulgaris</i> , <i>Cinnamomumtamala</i> , <i>Cinnamomum-verum</i> , <i>Brassica oleracea</i> var. <i>Italica</i>	50 mL of the extract were heated to 60–70 °C and then 5 g of Zinc nitrate was added to it when the temperature reaches 60 °C	Zinc oxide	20 ± 2 30 ± 3 46 ± 2 47 ± 2	Spherical Rod shaped Spherical Spherical	Antimicrobial activity	(Pillai et al. 2020)
Zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$	<i>Nelumbonucifera</i> (lotus) leaf	0.1 M aqueous solution was prepared by adding 0.595 g of zinc nitrate, $Zn(NO_3)_2 \cdot 6H_2O$ in 20 ml of DI water	Zinc oxide	3–4	Spherical		(Narayana et al. 2020)

Table 3 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Zinc nitrate	<i>Aloe barbadensis</i> miller leaf	Under continuous stirring with a magnetic stirrer, zinc nitrate was dissolved in the aloe extract solution with varying concentrations	Zinc oxide	25–40	Spherical	Biomedical and cosmetic	(Sangeetha et al. 2011)
Zinc acetate dihydrate	Flower extract of <i>Nyctanthes arbor-tristis</i>	Flower extract was added to a 50 mL zinc acetate solution in amounts of 0.25 mL to 2 mL while stirring continuously	Zinc oxide	12–32		Antifungal activities	(Jamdagni et al. 2018)
Zinc acetate	Leaves extract of <i>Laurus nobilis</i>	25 mL of 0.02 M Zn(OAc) <sub>2</sub> ·2H <sub>2</sub> O solution was mixed with 1 mL of the leaves extract	Zinc	21.49	Bullet like structure		(Fakhari et al. 2019)
Zinc acetate dehydrate	<i>Hibiscus subdariffa</i> leaf extract	After heating 20 ml of plant extract at 50 °C for 10 min, 50 ml of 91 mM zinc acetate solution was added dropwise to it while stirring	Zinc oxide	12–46 (diameter) 190–250 (length) 50–60 (breadth)	Dumbell shaped	Antibacterial activity	(Bala et al. 2015)
Zinc nitrate hexahydrate (Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O)	<i>Moringa oleifera</i>	10 mL of <i>M. oleifera</i> leaf aqueous extract was boiled at 60–80 °C by using magnetic stirrer. When the temperature reached at 60 °C, 2 g of zinc nitrate hexahydrate (Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O) was added	Zinc oxide	15–20	Spherical	Antimicrobial activity	(Elumalai et al. 2015)
Zinc nitrate hexahydrate	<i>Eucalyptus globulus</i>	20 mL of leaves extract was mixed with 20 mL of 0.1 N Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O aqueous solution	Zinc oxide	11.6	Spherical	Photocatalytic activity (degradation of methylene blue and methyl orange)	(Siripreddy and Mandal 2017)

Table 3 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Zinc acetate	<i>Ulva lactuca</i> seaweed extract	5 ml of the extract was added to the aqueous solution of 1 mM zinc acetate (95 ml) under continuous stirring and heating at 70 °C for 3–4 h	Zinc oxide	10–50	Assymetrical	Bactericidal activity	(Ishwarya et al. 2018)
Zinc nitrate hexahydrate [Zn(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O]	<i>Chironji (Buchanania lanzan)</i> leaves	With 10 ml of distilled water, a stoichiometric volume of Zn(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O was dissolved with 0.2 g of B. lanzan leaf extract	Zinc oxide	6–11		Photocatalytic activity (photodegradation of malachite green)	(Suresh et al. 2015)
Zinc nitrate hexahydrate [Zn(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O]	<i>Punica granatum</i> L and <i>Tamarindus indica</i> L	10, 11 and 12 mL of aqueous extracts of both the fruits were added to zinc nitrate hexahydrate [Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O] (3gm in distilled water)	Zinc oxide nanopowder	4–20		Antibacterial and anticancer properties	(G.K. et al. 2015)

Table 4 Examples of copper/copper oxide nanoparticles synthesis

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Copper sulphate	<i>Mitragynaparvifolia</i> Plant Bark	10 mL of extract added to 90 mL of an aqueous copper sulphate solution	Copper	23.6–41.2	Spherical	Antibacterial activity	(Kotval et al. 2018)
Copper sulphate	<i>Perseaamericana</i> seeds	20 ml of seed extract was added with 80 ml of CuSO <sub>4</sub> solution	Copper	42–90	Spherical	Antifungal and antioxidant activity	(Rajeshkumar and Rinita 2018)
Copper nitrate	L-ascorbic acid and chitosan	10 ml of 0.2 M copper nitrate solution was mixed with 4 ml of 1% w/v chitosan and 4 ml of 1 M ascorbic acid	Copper oxide	5.1–0.2	Spherical	Antibacterial activity	(Vázquez et al. 2019)
Copper acetate	<i>Millettiapinnata</i>	3 ml of the extract added to 40 mL of 1 mM Cu <sub>2</sub> (OAc) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> solution	Copper	13–35	Spherical agglomerates	Medicinal properties	(Thiruvengadam et al. 2019)
Copper sulphate	<i>Falcaria vulgaris</i> leaf	Leaf extracted was added to CuSO <sub>4</sub> (0.04 M) and L-Ascorbic acid (0.001 M) solution	Copper	20–25	Spherical	Non-cytotoxicity, antioxidant, antifungal, antibacterial activity	(Tahvilian et al. 2019)
Cupric nitrate trihydrate	<i>EryngiumcaucasicumTrautv</i>	10 mM 50 ml of cupric nitrate trihydrate (Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O) mixed with 5 ml of aqueous extract	Copper	40	Spherical	antioxidant and antimicrobial activity	(Hasheminya and Dehghannya 2019)
Copper sulphate	<i>Allium saralicum</i> leaves	CuSO <sub>4</sub> (0.04 M) and L-Ascorbic acid (0.001 M) solutions were added to A. saralicum extract	Copper	45–50	Spherical	Antioxidant, antibacterial, antifungal, and cutaneous wound healing potentials	(Tahvilian et al. 2019)
Copper sulphate	<i>Punicagranatum</i> leaf	0.2 M CuSO <sub>4</sub> solution was added to the extract in a ratio of 1:2 (v/v)	Copper oxide	20.33	Spherical	Adsorbent properties (dye removal)	(Vidovix et al. 2019)



Table 4 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Copper sulfate pentahydrate	<i>Citrus medica</i> Linn	Specific volume of filtered extract was added to aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mM)	Copper	10–60		Antimicrobial activity	(Shende et al. 2015)
Copper (II) Sulfate Pentahydrate	Ascorbic acid, native cyclodextrins	Aqueous solutions of ascorbic acid (1.09 g/25 mL $\text{H}_2\text{O}$ ) and native cyclodextrin (0.25 g/25 mL $\text{H}_2\text{O}$ ) were added dropwise to aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.3975 g/25 mL $\text{H}_2\text{O}$ ) under constant heating and stirring	Copper	2–33	Spherical		(Suárez-Cerdá et al. 2017)
Cupric chloride dihydrate	<i>Azadirachta indica</i>	Leaf extracts were added dropwise to the aqueous solution of salt $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ( $7.5 \times 10^{-3}$ M) under constant heating through oil bath and magnetic stirring	Copper	48	Cubic		(Nagar and Devra 2018)
Cupric acetate	<i>Syzygium aromaticum</i> (clove) bud	10 ml of aqueous extract of <i>Syzygium aromaticum</i> bud was added to 50 ml of 0.001 M of cupric acetate solution and mixed homogeneously on magnetic stirrer	Copper	20	Spherical	Antibacterial properties	(Rajesh et al. 2018)
Copper sulfate	Fish scales of <i>Labeo rohita</i>	At a pH of 9, 0.5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 10 g of double-distilled water, and 50 ml of 10% fish scale extract was added	Copper	25–37	Spherical	Photocatalytic degradation of Methylene Blue	(Sinha and Ahmaruzzaman 2015)

Table 4 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Copper sulfate pentahydrate	Seedless dates	0.1 g copper sulphate pentahydrate was dissolved in 10 mL deionized water and dropped into the dates extract and Cetyl trimethylammonium bromide mixture dropwise	Copper and copper oxide	78	Spherical		(Mohamed 2020)
Copper sulfate	Fruit extracts of <i>Ziziphus spina-christi</i> (L.) Willd	Fresh fruit extract were added to the CuSO <sub>4</sub> (0.02 M) solution containing starch	Copper	5–20	Spherical	High adsorption capacity and antibacterial activity	(Khani et al. 2018)

in packaging materials for food and medicines as it possesses antimicrobial properties (Zare et al. 2017). Nanoparticles also help in enhancement of different food processes, packaging materials and preservation of various food items. Different technologies which makes use of nanomaterials for analytical study, helps in maintaining and controlling the quality of food materials (Chaudhry et al. 2018). In one of such example, bacterial nano cellulose was synthesized by incorporation of silver, palladium and copper nanoparticles, out of which silver bacterial nano cellulose showed impressive antibacterial activity and can be used for food packaging material (Razavi et al. 2020). Nanoencapsulation technique is widely used in food industry to improve the stability of food constituents, enhance the taste, maintaining the pH and to protect the food against oxidative agents. This technique makes sure that the encapsulated component reaches its destination safely even in harsh environments and hence nanoencapsulation is used to deliver various nutrient and health supplements like vitamins and minerals. Various sweeteners, crèmes, flavored oils, salad dressings and beverages are prepared using nanoemulsions. To check over the microbial growth and reduce the spoiling of food items, nanoemulsions made out of tributyl phosphate with soybean or other nonionic surfactant (Hamad et al. 2018).

### Antimicrobial activities

The Ag NPs produced via green synthesis methods have been shown to be able to destroy the polymeric subunits of the cell membrane in case of the pathogenic organisms, thus, breaking the cell membrane and disturbing the protein synthesis mechanism of the bacteria (Kuppusamy et al. 2016). Hence, silver NPs are used as antibacterial agents. The interactions of metallic gold and silver NPs and bacteria have been to inhibit cell cycle functions by binding with the active site of cell membrane (Kim et al. 2007). The zinc oxide nanoparticles which were synthesized from the floral extracts of *Trifolium pretense* showed inhibitory response against various bacterial strains like *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. Also these ZnO nanoparticles were ascribed for inhibiting and killing the microbial cells by damaging the cell wall and expulsion of cytoplasmic material (Dobrucka and Długaszewska 2016). The main reason behind the inhibition and killing of bacterial cells is the formation reactive oxygen species (ROS) by the nanoparticles. The ROS like hydroxyl radicals, singlet oxygen and hydrogen peroxide, damages the bacterial cell wall, ribonucleic acid, proteins or intracellular organelles when it comes in contact with it producing Zn<sup>2+</sup>. Due to these properties Zn nanoparticles are used in packaging materials of edible items and pharmaceutical products. Also, they are incorporated in polyurethane films as they helps in the enhancement of its tensile strength and Young's

**Table 5** Examples of iron/ iron oxide nanoparticles synthesis

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )	<i>Moringa oleifera</i>	The extracts of different concentrations were mixed with 0.1 M $\text{FeCl}_3$ solution with various volume ratios of 1:1, 1:2, 1:3 and 1:4	Iron	250–474	Spherical	Coagulant and antibacterial activities (nitrate removal)	(Katata-Seru et al. 2018)
Ferric chloride ( $\text{FeCl}_3$ )	<i>Hibiscus sabdariffa</i> , <i>Roselle</i> flower aqueous extract (HBS)	5.0 cm <sup>3</sup> flower extract was added in a reaction mixture containing 0.01 mol dm <sup>-3</sup> of $\text{Fe}^{3+}$	Iron	18–44	Spherical	Catalytic and antimicrobial activity	(Khan and Al-Thabaiti 2018)
$\text{FeCl}_3$	<i>Nephrolepisauriculata</i>	Addition of the extract to 20 mL of $\text{FeCl}_3$ solution (0.1 M) with a 2:1 volume ratio	Iron	40–70	Spherical	Catalytic activity (Cr(VI) removal)	(Yi et al. 2019)
$\text{FeCl}_3$ and $\text{FeSO}_4$	<i>Pandanus odoratissimus</i> leaves	5.0 mL of extract added to 4.0 mL of 0.1 M $\text{FeCl}_3$ followed by the drop wise addition of 2 mL of 0.1 M $\text{FeSO}_4$ in the molar ratio of 2:1 of $\text{Fe}^{3+}$ : $\text{Fe}^{2+}$	Iron oxide ( $\text{Fe}_3\text{O}_4$ )	5.0	Spherical	Electro-catalysts	(Alajmi et al. 2018)
Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )	<i>Teucriumpolium</i> leaves	1 ml $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.1 M added to 9 ml leaf extract	Iron oxide	5.68–30.29	Spherical	Catalytic activity (catalyzed $\text{H}_2\text{O}_2$ on the degradation of methyl orange)	(Kouhbanani et al. 2019)
Iron(II) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )	Peanut skin	0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (100 mL) solution was added to the extract (300 mL), under a nitrogen atmosphere	Iron	30–100	Spherical	Reduction and adsorption activity (Cr(VI) removal)	(Pan et al. 2019)
Iron(II) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )	Plantago major leaves	1 ml of 0.1 M aqueous mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , was added to a 9 ml leaf extract	Iron oxide	4.6–30.6	Spherical	Catalytic activity (degradation of azo dyes)	(Lohrasbi et al. 2019)
Iron sulphate	Green tea and eucalyptus leaves extracts	At room temperature, leaves extracts were added to 0.10 M $\text{FeSO}_4$ in a 2:1 volume ratio and stirred continuously for 30 min	Iron	20–80	Quasi spherical	High adsorptivity (Nitrate removal from waste water), high stability	(Wang et al. 2014b)

Table 5 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Iron(III) nitrate nonahydrate	<i>Eucalyptus urophylla</i> and <i>Eucalyptus grandis</i>	Under N <sub>2</sub> protection, 250 mL of 0.1 M FeNO <sub>3</sub> ·9H <sub>2</sub> O solution was introduced dropwise to a 1000 mL three-necked flask containing 500 mL of leaf extract and stirring at room temperature for 30 min before being centrifuged at 10,000 rpm for 8 min	Iron	10.69	Plates	Adsorbivity (removal of Arsenic)	(Wu et al. 2019)
Iron sulfate	Green tea, oolong tea, and black tea extracts	A 1:2 volume ratio of 0.1 mol/L FeSO <sub>4</sub> solution was added to the filtered tea extracts	Iron	20–40	Spherical	Catalysis (Fenton-like oxidation of monochlorobenzene)	(Kuang et al. 2013)
Ferrous sulphate heptahydrate	<i>Azadirachta Indica</i> leaf extract	Separately, 10 ml of leaf extract was combined with 2 ml of 0.1 M FeSO <sub>4</sub> metal salt in the ratios of 1:5, 1:4, 1:3, 1:2, and 1:1	Iron	120–600	Spherical	Antibacterial activity	(Devatha et al. 2018)
Iron chloride hexahydrate	<i>Dimocarpus longan</i>	With a volume ratio of 1:2, FeCl <sub>3</sub> solution (0.1 M) was added to the plant extract solution (60 g/L), followed by homogeneous stirring (200 rpm) at room temperature for 1 h	Iron	5	Spherical	Catalysis (degradation of methylene orange)	(Yuan et al. 2020)
Ferric chloride hexahydrate	<i>Mediterranean cypress</i> ( <i>Cupressus sempervirens</i> )	1 mL FeCl <sub>3</sub> ·6H <sub>2</sub> O (1 M) was added to Leaf extract (9 mL) and stirred vigorously at room temperature for 24 h	Iron	9–31		High adsorbivity and catalytic activity	(Ebrahimezhad et al. 2018)



Table 5 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Ferric chloride	Carob pod ( <i>Ceratonia siliqua</i> )	The extract was added to 3.8 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ferric chloride solution at a 1:1 volume ratio while continuous mixing on a magnetic hot plate	Iron oxide	$5 \pm 7$	Spherical	Adsorption (removal of Beta-lactam antibiotic amoxicillin)	(Aksu Demirezen et al. 2019)
Ferric chloride	Tangerine peel extract	In the presence of extract peel as a surfactant and stabilizing agent, 5.35 g of $\text{FeCl}_3$ and 8.10 g of $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ were separately dissolved in 500 ml of varying concentrations of extract peel to form a solution with a concentration of 0.1 M for Fe(III) and Fe(II)	Iron oxide	50–200	Spherical	Adsorption (cadmium ion removal)	(Ehrampoush et al. 2015)

Table 6 Examples of palladium nanoparticles synthesis

Material precursor	Reducing agent used	Amount of extract	Size of nanoparticle (nm)	Morphology	Properties	References
Palladium chloride	<i>Spirulina platensis alga</i>	10 mL of alga extract was added to 50 mL of 1 mM PdCl <sub>2</sub> solution	10–20	Spherical	Adsorption (lead removal)	(Sayadi et al. 2018)
Palladium acetate	Black pepper ( <i>Piper nigrum</i> )	50 mL 10 mM Pd(OAc) <sub>2</sub> stirring at 85 °C, 10 mL of black pepper extract was added drop wise	2–7	Spherical	Catalytic activity (aryl halide cyanation, Hiyama cross-coupling)	(Kandathil et al. 2018)
Palladium chloride	Bark of <i>Terminalia arjuna</i>	mixture of palladium chloride solution (0.4 mL, 5.019 mM) and the bark extract heated at 60–70 °C for 2 min	4–16	Spherical	Catalytic activity (reductive degradation of dyes)	(Garai et al. 2018)
Palladium chloride	<i>Lantana camara</i> plant	0.4 ml of 0.01 M aqueous PdCl <sub>2</sub> solution was added drop wise to 2.0 ml of 0.4 wt% aqueous extract solution	5.1	Spherical	Catalytic activity (towards Suzuki-Miyaura cross-coupling reaction)	(Phukan et al. 2019)
Palladium chloride	<i>Ananas comosus</i> leaf	20 mL of <i>A. comosus</i> leaf broth was added to 80 mL of the 2 mM aqueous PdCl <sub>2</sub> solution	1.74–16.14	Spherical	Photocatalytic activity (degradation of polyethylene film)	(Olajire and Mohammed 2019)
Palladium chloride	<i>Nonpareil almond</i> hull	Nonpareil almond hull extract (2.5% w/v) (2 mL) was added to a aqueous solution of PdCl <sub>2</sub> (10 mg PdCl <sub>2</sub> was pre-dissolved in 10 mL water)	> 20	Spherical	Catalytic activity (reduction of R6G, MO and MB by NaBH <sub>4</sub> )	(Rashidi et al. 2019)
Palladium chloride	Cottonboll peels	30 mL plant extract added to 15 mL palladium chloride solution (5 mM)	4–20	Spherical	catalytic activity(reduction of the azo-dyes)	(Narasaiah and Mandal 2020)
Palladium acetate	<i>Rosmarinus officinalis</i> leaves	10 mL of leaf broth was added to 20 mL of the palladium acetate solution (0.1 M)	15–90	Semi-spherical	Antibacterial and anti-fungal activity	(Rabiee et al. 2020)
Palladium chloride	Urine of indigenous Indian <i>Khilar</i> cow	50 mL of cow urine drop wise added to 200 mL of 0.01 M PdCl <sub>2</sub> solution	16.93–19.27	Hexagonal	Antimicrobial ad free radical activity (medical use)	(Prasad et al. 2020)
Palladium chloride (PdCl <sub>2</sub> )	<i>Cinnamomum camphora</i> leaf extract	To obtain 1 × 10 <sup>-3</sup> mol L <sup>-1</sup> , 3 × 10 <sup>-3</sup> mol L <sup>-1</sup> , and 5 × 10 <sup>-3</sup> mol L <sup>-1</sup> PdCl <sub>2</sub> solutions, an appropriate volume of concentrated aqueous PdCl <sub>2</sub> solution (0.226 mol L <sup>-1</sup> ) was added to 50 ml filtrate at room temperature	3.2–6	Spherical	Catalytic activity	

Table 6 (continued)

Material precursor	Reducing agent used	Amount of extract	Size of nanoparticle (nm)	Morphology	Properties	References
Palladium chloride	<i>Chlorella vulgaris</i> alga	Then about 50 mL aqueous solution of 1 mM palladium chloride (PdCl <sub>2</sub> ) was mixed with 10 mL of crude extract	5–20	Spherical		(Arsiya et al. 2017)
Palladium chloride (PdCl <sub>2</sub> )	<i>Sargassum bovinum</i>	Around 50 mL of 1 mM palladium chloride (PdCl <sub>2</sub> ) aqueous solution was combined with 10 mL of crude extract	5–10	Octahedral	Catalytic activity	(Momeni and Nabipour 2015)
Palladium chloride	<i>Anogeissus latifolia</i>	The gum solutions containing PdCl <sub>2</sub> were autoclaved at 121 °C and 103 kPa for 30 min	4.8 ± 1.6	Spherical	Antioxidant and catalytic activity	(Kora and Rastogi 2018)
Palladium chloride	<i>Hippophae rhamnoides</i> Linn leaf extract	With continuous stirring at 80 °C, 10 mL of leaf extract was introduced dropwise to 50 mL of 0.003 M aqueous PdCl <sub>2</sub> solution	10	Spherical	Catalytic activity	(Nasrollahzadeh et al. 2015)
Palladium chloride	Carboxymethyl cellulose sodium salt	In a 10 mL flask, PdCl <sub>2</sub> solution (10 mM) and Carboxymethyl cellulose aqueous solution (1.0 wt%) were combined	2.5	Spherical	Catalytic activity (degradation of azo dyes)	(Li et al. 2017)

**Table 7** Examples of titanium oxide nanoparticles synthesis

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Titanium Isopropoxide	<i>Ocimumbasilicum</i>	10 ml of Titanium Isopropoxide (TTIP) was added drop wise to 250 ml of distilled water and the extract was added to this solution till the solution achieves a pH of 7	Titanium dioxide	100–120	Tetragonal	Antibacterial and insect repellent activities	(Alapati and Kantheti 2018)
Titanium tetra (isopropoxide)	<i>Eucalyptus globulus</i> leaf	Titanium tetra (isopropoxide) (3 mL) was dissolved in ethanol (50 mL), and 50 mL of the plant extract solution was added to it dropwise in the ratio of 1:1 (v/v)	Titanium dioxide	12	Anatase	Catalytic activity	(Balaji et al. 2019)
Titanium(IV)-iso-propoxide	<i>Carica papaya</i> leaves	40 ml of 0.5 M of TTIP was added to 40 ml of extract in a ratio of 1:1 (v/v)	Titanium dioxide	15.6	Spherical	Photocatalytic activity (photo degradation of RO-4 dye)	(Kaur et al. 2019)
Titanium isopropoxide (TTIP)	<i>Cajanuscajan</i>	90 ml of 5 mM TTIP solution (precursor) was added to 30 ml of pulse extract (reducing agent) in the ratio of 9:3 (v/v)	Titanium dioxide	10–25	Anatase	Membrane antifouling property	(Arif et al. 2019)
Titanium tetra chloride	Orange peel	1 M of Titanium tetra chloride was added to 100 mL of deionised ice to which 10 mL of extract was added slowly	Titanium dioxide	20–50	Triangular	Antibacterial activity	(Mobeen Amanulla and Sundaram 2019)
TiO <sub>2</sub> bulk powder	Lemon peel	1.25 g of titania bulk powder added to the 2.5 ml distilled water and 35 ml of the lemon peel extract was mixed gradually	Titanium dioxide	80–140	Spherical	Photo catalytic activity	(Nabi et al. 2020)

Table 7 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Titanium dioxide	<i>Allium eriophyllum</i> Boiss	Plant extract was added to a 1 mM TiO <sub>2</sub> solution in different ratios and stirred at room temperature; after colour shift, the solution was centrifuged for 15 min at 12,000 rpm	Titanium	22	Spherical	Non-cytotoxic, anti-oxidant, antibacterial, antifungal and cutaneous wound healing	(Seydi et al. 2019)
Titanium oxy sulphate	<i>Trigonella foenum-graecum</i> leaf extracts	15 mL of the extracts was added to 0.5 M solution of Titanium oxy sulphate and stirred for 15 min	Titanium dioxide	20–90	Spherical	Antimicrobial activity	(Subhapiya and Gomathi priya 2018)
Titanium dioxide	<i>Echinacea purpurea</i> herba	At 25 °C, 10 mL of the aqueous extract was added to 20 mL of 1 mM TiO <sub>2</sub> and stirred for 4 h	Titanium dioxide	120	Spherical		(Dobručka 2017)
Titanium dioxide	<i>Azadirachta indica</i> leaf extract	At 25 °C, 10 mL of the aqueous extract was added to 20 mL of 1 mM TiO <sub>2</sub> under constant heating at 60 °C and stirred for 4 h	Titanium dioxide	15–87	Spherical	Antimicrobial activity	(Thakur et al. 2019)
Titanium dioxide	<i>Sesbania grandiflora</i>	25 mL extract was combined with 225 mL of a 5 mM titanium dioxide (TiO <sub>2</sub> ) solution and incubated at room temperature for 24 h under light	Titanium dioxide	43–56	Triangular, square, spherical	Toxic nature	(Srinivasan et al. 2019)
Titanic acid	<i>Jatropha curcas</i>	1 mL crude latex was diluted to 300 mL and mixed with 2.5 mM aqueous TiO (OH) <sub>2</sub> solution in equal parts and heated at 50 °C for 10 min	Titanium dioxide	25–100	Spherical		(Hudlikar et al. 2012)

Table 7 (continued)

Material precursor	Reducing agent used	Amount of extract	Nanoparticle	Size of nanoparticle (nm)	Morphology	Properties	References
Titanium dioxide	<i>Myrtus communis</i> leaf extract	With continuous stirring at 80 °C for 2 h, 20 mL of the plant extract was added dropwise to 40 mL of a well-mixed solution of PdCl <sub>2</sub> (0.3 mM) and 1.0 g of Degussa P-25 TiO <sub>2</sub>	Pd/TiO <sub>2</sub>	17–25	Spherical	Highly efficient, stable, recyclable, catalysis	(Nasrollahzadeh and Mohammad Sajadi 2016)
Titanium (VI) isopropoxide	<i>Green alga Chlorella pyrenoidosa</i>	20 mL algal extract was introduced dropwise to a 0.5 M titanium (VI) isopropoxide solution, and the solution was maintained at 60 °C for 4 h with constant stirring	Titanium Dioxide (TiO <sub>2</sub> )	Spherical	50	Photo catalysis	(Sharma et al. 2018b)
Titanium dioxide	Leaves extracts of <i>Euphorbia heterophylla</i>	With continuous stirring at 60 °C for 2 h, 20 mL of the plant extract was added dropwise to 40 mL of a well-mixed solution of AgNO <sub>3</sub> (0.003 M) and 1.0 g of Degussa P-25 TiO <sub>2</sub>	Ag/TiO <sub>2</sub>	> 28		Catalysis (reduction 4-nitrophenol, Methyl orange, Congo red, Methylene blue)	(Atarod et al. 2016)



modulus (Shi et al. 2014)(Amini 2019). According to one of the analysis, green synthesized ZnO nanoparticles also possess antifungal properties for the fungal strains *Aspergillus flavus*, *Aspergillus nidulans*, *Trichoderma harzianum*, and *Rhizopus stolonifer* (Gunalan et al. 2012). In another example, copper nanoparticles were synthesized from the bud extract of *Syzygium aromaticum*. These biosynthesized nanoparticles showed remarkable antimicrobial activity against *Bacillus* species and antifungal activity against *Pseudomonas* species (Rajesh et al. 2018). According to the literature, metallic nanoparticles are effective against a variety of viruses and parasites. In comparison to chemically synthesized silver nanoparticles, herbally synthesized silver nanoparticles have demonstrated greater larvicidal efficacy against *Anopheles stephensi*, according to M. Santos et al. (Santos et al. 2018). Similarly, selenium nanoparticles which were synthesized using ascorbic acid as a reducing agent exhibited larvicidal activity against causative malaria vector *Anopheles stephensi* (Salem et al. 2021).

### Heavy metal ion sensing

Well-known contaminants in soil, air and water are various heavy metals, such as Ni, Cu, Pb, Co, Cr, Zn, Hg, Mn, etc. Different sources of these pollutants include vehicle emissions, dye industries, coal, plastic, natural gas and mining wastes (Zhang et al. 2012). Metals like cadmium, copper and lead show increased levels of toxicity even at very minute amounts (trace ppm levels) (Ahmad et al. 2010). The detection of toxic metals in both biological and marine settings has therefore become an important prerequisite for suitable corrective purposes. (Aragay et al. 2011). There are various techniques which have been conventionally used and they offer good sensitivity but the experimental setups are time consuming, skill dependent and highly expensive. Because of the distance dependent optical properties and the tunable size of the metal NPs, they are increasingly used in contaminated water systems for the identification of heavy metal ions. The advantages include high sensitivity at low ppm levels and low cost (Annadhasan et al. 2014). By using different plant derivatives for use as colorimetric indicators for heavy metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$ , etc., Ag NPs have been synthesized.. The silver NPs prepared from green tea extract and pepper seed extract displayed selective sensing properties for some ions (Karthiga and Anthony 2013). In another study silver nanoparticles which was stabilized by acacia lignin extract was used for constructing a probe for a colorimeter to analyze aqueous solutions of heavy metal. The interaction between the nanoparticles and metal ions was recorded using a UV-vis spectroscopy and showed different high and low peaks for different metal ion concentrations (Aadil et al. 2019). Due to the nanoscale size of nanoparticles, it is easy to incorporate them into new

compact devices for constructing probes and other sensing instruments and also they can be used for instant analysis and provides genuine results. Optical sensing, electrical and chemical sensing, biochemical sensing, and plus various sensing are the various types of nanomaterial-based sensing methods used for heavy metal ion sensing. Gold nanoparticles, quantum dots and nano metal organic structures are commonly used in optical sensing. Au nanoparticles have been used for mercury ion ( $\text{Hg}^{2+}$ ) detection in aqueous medium using a colorimetric assay. Nano metal organic frameworks are porous luminescent sensors and its aluminum based variant has also been used for  $\text{Hg}^{2+}$  ions sensing (Kumar et al. 2017). Electrochemical sensing consists of electrodes mainly based on metal nanoparticles, metal oxides, heteroatoms and ternarynanocomposites. In one of the example, a nanocomposite based glassy carbon electrode was used for the electrochemical suspicion of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  (Zuo et al. 2019).

### Elimination of pollutant dyes

Organic dyes (cationic and anionic) play a very important role as they have a huge demand in industries like textiles, leather, food, printing, plastic, pharmaceutical and paper mills. Almost 15 percent of the dyes get discarded after the fabric process is finished and they are released into the water bodies and cause substantial contamination due to their aggressive behavior. These contaminants are basically a hazard since they create unwanted water turbidity that limits the penetration of sunlight, thereby hampering aquatic life by preventing photochemical synthesis. (Singh et al. 2018). Hence, management of these dyes containing effluents is a major task. The superior photocatalytic activity of the semiconductor nanoparticles like ZnO,  $\text{TiO}_2$ , magnesium oxide (MgO), etc., is being increasingly used for oxidizing the toxic pollutants. Their property is result of the high surface to mass ratio that promotes organic pollutant adsorption. (Thiruvengadam et al. 2019). The surface energy of the nanoparticles increases due to the large number of reactive sites available on the surface, which contributes to an improved rate of removal of pollutants at low concentrations. Therefore, relative to high volume of materials, a smaller number of nanoparticles would be needed for water treatment. (Dror et al. 2005). Nickel sulphide nanoparticles were the first one to be reported for the successful removal of organic dyes like methylene blue and safranin O. In one of the example Reactive black 5 and sodium dodecylbenzenesulfonate was reported to be removed from its aqueous solution using amino functionalized silica nanoparticles. Methylene blue dye was successfully removed to a great extent when amino rich zirconium based magnetic metal organic framework composites were used for the same (Hlongwane et al. 2019). Asiman Dash et al. 2019 reported the synthesis

of  $\text{Fe}_3\text{O}_4$  nanoparticles from the pod extract of *Peltophorum pterocarpum*. These nanoparticles showed mesoporous structure and large surface area which made them a potential candidate to remove various dyes through adsorption; also it successfully removed methylene blue from its aqueous solution up to a adsorption potential of 88.98% (Dash et al. 2019).

## Conclusion

### Sustainable impact

Chemical synthesis of nanoparticles may require implementation of several chemical ligands or functional groups like thiols, phosphines or polymers and toxic surfactants like cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), decyltrimethylammonium bromide (DTAB) and tetradecyltrimethylammonium bromide (TTCB) for stability of the so formed nanoparticles and controlling their size and shape. These chemicals lead to the production of harmful byproducts during the synthesis process. When plant extracts are used for the same, there is occasional use of any chemicals to stabilize the product or to control the shape or size. Green synthesis provides a sustainable production of nanomaterials without producing any kind of toxic and noxious chemicals i.e. its main aim is to focus on a process which is more reliable, economic, safe, efficient and sustainable because sustainability is to meet the need but perpetuating the balance between society, economy and environment. Few examples for the same involves, the rapid formation of phase pure magnesium ferrite nanoparticles at low temperature, low cost, using eco-friendly deep eutectic solvent systems and metal oxides as the precursors (Baby et al. 2020), formation of silver nanoparticles using leaves extracts of *Ekebergiacapensis* which is an agroforestry residue and can biodegrade food based azo-dyes (Anand et al. 2017), production of such nano materials through chemical synthesis can produce a large quantity of toxic byproducts, consuming a huge amount of energy and is expensive. Green synthesis allows the production of metal nanocatalysts like Ag, Pd, Au, Cu, Ce, Ni, Ru, etc. utilizing biodegradable adsorbents or supports such as chitosan, cellulose or by using recyclable magnetic ferrites (Smuleac et al. 2011). In one of the example, organocatalysts was prepared from nanoparticles and green synthesis. This catalyst was later used for catalyzing Paal-Knorr reaction in pure aqueous solvent with an excellent yield due to which there was no need to make use of any toxic solvent. In another example, green synthesized magnetic ferrite nanoparticles were modified with dopamine and then used as a base for hydration of benzonitrile with ruthenium hydroxide which catalyzes the reaction. Once the reaction was completed,

the ruthenium hydroxide was deposited over the nanoferrite rod due to its paramagnetic nature and lead to easy separation of catalyst and reduction in further separation processes (Varma 2012). Implication of such processes results in decreased waste products and allows us to proceed on the path of green engineering.

### Biodiversity

Nature has designed the nanostructures in such a way that it wonderfully impacts at macroscopic level. The different morphological colors, scaling patterns, radiance, luminescence, shiny and bright appearances at macroscopic range in nature is due to the arrangement of components at nanoscale (Dumanli and Savin 2016). The concept of biomimicking is a novel approach in nanobiotechnology, mimicking nature in a productive manner, upgrading the current technology and fulfilling the need in a more sustainable way. The rich biodiversity of the plant kingdom offers us a huge number of examples to biomimic for the betterment of our technologies. Nanoimprint lithography is a technique to produce 3D structures and fabrication of these nanoscale structures over high resolutions with great accuracy. Using this technique a biomimic of Morpho butterfly was created and then coated with titanium oxide and silicon oxide via electron beam deposition to create exact refractive index contrast. Biomimicry of natural colour patterns like in butterflies, flowers, nacre, opals or pearls is created by many paint industries using acrylic based paints by the incorporation of mica nanoflakes and sometimes added with an extra coating of metal oxides of titanium or iron oxide for a sparkling dazzle finish (Dumanli and Savin 2016). Green synthesis can make use of any simple prokaryotic bacteria or complex eukaryotes or small plants which are easily accessible or rare plant species, for the reduction of metal ions, also all these help us to explore more options to produce nanoparticles in an eco-friendly way. Plant extracts are used widely as compared to bacteria and fungi for their high synthesis rate, good capping ability and also it provides a stable product. Also the same nanoparticle can be synthesized from different plant extracts. Examples include synthesis of silver nanoparticles from leaf extracts of *Ficus benghalensis*, *Argemone mexicana*, carob leaf, *Jatropha curcas*, synthesis of gold nanoparticles from leaf extracts of *Dalbergiacoromandeliana*, *Croton Caudatus Geisel*, *Thymus vulgaris*, synthesis of zinc nanoparticles from plant extracts of *Carica Papaya*, *Tecomacastanifolia*, *Rhamnusvirgata*, etc. and many more.

### Nanoparticle toxicity and safety risks

Concerns over the nanoscale materials' unintended health and environmental effects have grown in tandem with their current and evolving use. Exposure evaluation, toxicology,

extrapolation, biological and environmental fate, transportation, longevity, transition, and overall survival are all important risk assessment concerns for engineered nanomaterials (Jeng and Swanson 2006). Owing to their peculiar physicochemical properties e.g., nano scale, large surface area proportion, elemental composition, electronic properties, crystal structure, reactivity and functional groups, inorganic or organic coatings, solubility, structure, and aggregation behavior, nanoparticles have the ability to cause adverse effects on organ, tissue, cellular, sub-cellular, and protein levels. Due to their extensive medical, automotive, industrial, and defense uses, metal NPs have attracted a lot of attention. These metal-based nanoparticles, on the other hand, have been shown to be extremely toxic, despite the fact that the same element is comparatively harmless in its bulk form (Sengupta et al. 2014). Magnesium oxide, chromium nanoparticles decorated with cobalt, and manganese nanoparticles are cytotoxic to mammalian cells and have also been used to treat cancer. It has also been discovered that it produces reactive oxygen species, which leads to apoptosis. Nanostructures can enter deep into the body, have a wider surface area due to their small size, and have a charge on their surface, causing a greater inflammatory reaction. (Sengupta et al. 2014). Researchers were required to create more biocompatible nanostructures due to the lack of biodegradability and toxicity of certain metallic and oxide nanoparticles. For the development of biocompatible metal NPs, green synthesis using plant biomass or extracts or other biological entities is a viable option. As a whole, the literature on the confirmed toxicity of metal NPs synthesized using plant extract is ambiguous. Both silver nanoparticles synthesized from *Caesalpinia pulcherrima* leaf extract (Moteriya and Chanda 2020) and ZnS nanoparticles produced by pyrolysis (Dash et al. 2014) demonstrated possible cytotoxicity and mild genotoxicity. On the other hand metal nanoparticles fabricated using garlic or tea extract have been shown to have a non-toxic effect (Amini and Akbari 2019). Surface chemistry is an essential aspect that determines not only the different uses of nanoparticles, but also the stability of synthesized nanoparticles. In addition to nanoparticles made with other chemical reductants such as citrate or sodium borohydride, phenolic compound coated metal nanoparticles are more stable (Amini 2019). However, in addition to stability, the coating gives the nanoparticles toxic properties, making them suitable for use in pharmaceuticals, biochemical, or antimicrobial formulations. The research found that cobalt ferrite nanoparticles increased oxidative stress in various cell lines and had dose-dependent cytotoxicity. In another study, copper nanoparticles induced cell growth inhibition by inducing oxidative stress, protein and DNA damage, and cell membrane damage (Sengupta et al. 2014). In case of zinc oxide nanoparticles smaller ligand capping on ZnO nanoparticles contributes to increased levels of

toxicity, and various surface functionalities of ZnO nanoparticles leads to improvements in particle size and decay of the nanoparticle in HepG2 cell culture (Sengupta et al. 2014). Thus, a holistic view of nanoparticles development and implementation, such as pharmacology, bioavailability, and side effects of therapeutics using nano composites, as well as the safety and efficacy of nanoparticles pre and post conjugation and toxicity is needed to incorporate these particles into our daily lives. Surface modulation, green synthesis, and conjugations should all be considered when creating toxin free nanoparticles.

### Future aspect

Green synthesis processes have the potential to bridle the demerits of conventional synthesis processes of nanoparticles. Nanoparticles produced by this route shows numerous properties some of which are high corrosion resistivity, stable in oxidative environments, antifungal, antiviral and antimicrobial behavior, optoelectronic, magnetic and catalytic properties etc. Considering these properties nanoparticles are being employed in all sectors whether in medical instruments, electronic gadgets, pharmaceuticals or food industry (Mahmoud 2020). The demand for nanomaterials is increasing and there is a need for an efficient process for production. Nanoparticles synthesis using green synthesis is still in its infancy and need to scale up from lab scale to industrial level. Also, there are several nanoparticles which require experimental attention for their implicational improvement. One of the examples is a desired type of rod or branched shaped Au nanoparticle which is majorly used in phototherapy or drug delivery in biomedicine is synthesized by using toxic surfactants like CTAB or CTAC. New green techniques for the synthesis of such nanoparticles must be discovered to expand their application (Heuer-Jungemann et al. 2019). The toxicity of metal nanoparticles must be assessed before they can be used in medical applications. The majority of researchers do not look at the toxicity of their biogenic nanoparticle. For the future use, a range of proper and comparative studies among biogenic and chemically synthesized metal nanoparticles are needed. Also, it is still difficult to control the size and shape of nanoparticles through this method. The behavioral process needs to be studied, to understand the functional groups and phytochemicals involved in biogenic production of nanoparticles and reduction mechanism and responsible components that are involved in the reduction process.

**Authors contribution** Pranali studied and collected all the papers related to the general mechanism for the reduction processes involved in the synthesis process. Rohit studied and collected all the papers related to the different examples and biological sources and different approaches and methods for the synthesis of metallic nanoparticles via

Green synthesis. S.M.Kodape studied and collected papers related to sustainability and environmental impact of Green synthesis. All authors have read and approved the final manuscript.

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