The Biogenic Synthesis of Au, Pd and Pt Nanoparticles and Its Medicinal Applications

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A Review

By

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CHAPTER ONE

INTRODUCTION

The prefix “nano” derives from the Greek word “nanos” signifying “dwarf” (one billionth of a meter 10^{-9}m), it is a term that has become common in scientific literature. Today “Nano” is a popular term commonly used in modern science and also appearing in dictionaries: for example, nanoscience, nanowire, nanotube, nanotechnology, nanostructure, nanoscale, nanometer, nanorobot, etc. The idea of nanotechnology producing nanoscale objects and nanoscale manipulations has been current for quite some time; the birth of the concept usually being linked to a speech by Richard Feynman at the December 1959 meeting of the American Physical Society [101] where he asked: “What would happen if we could arrange the atoms one by one the way we want them?”

The natural world abounds with examples of nanoscale structures, such as milk (nanoscale colloid), proteins, bacteria, cells, viruses, etc. Furthermore, many materials have a complex structure at the nanoscale state while appearing simple and smooth to the naked eye [Fig. 1.1].

A nanometer denotes one billionth of a meter or 10^{-9} m. Micro has come to mean anything small, while “nano” emphasizes unique phenomena observed in the nanoworld with atomic granularity. A new vocabulary has emerged from nano research, some important terms and concepts are presented below.

Nanotechnology: includes designs, synthesis (organic synthesis, biological synthesis, green synthesis etc.), and applications of material (industrial, biological, medicinal, therapeutic, etc.), and devices engineered at the nanoscale (size and shape). It exhibits unique chemical, physical, electrical, biological and mechanical properties that emerge in the form of matter at the nanoscale.

Nanoscience: The study of the phenomena at 1-100 nm.

Nanomaterial: are materials that have structured components containing at least one dimension less than 100 nm.

Nanoparticles: are nanosized structures in which at least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range (1 to 100 nm). Nanoparticles possess crystalline or amorphous forms that play an important role as carriers for droplets or gases and which pass organ barriers: e.g. blood-brain barriers.

Nanoparticulate matter: a collection of nanoparticles emphasizing their selective behavior.

1. Nanoparticle classification

Nanoparticles are mainly classified according to their composition, dimensionality, morphology, uniformity and agglomeration.

1.1. Dimensionality

1.2. Nanoparticle morphology

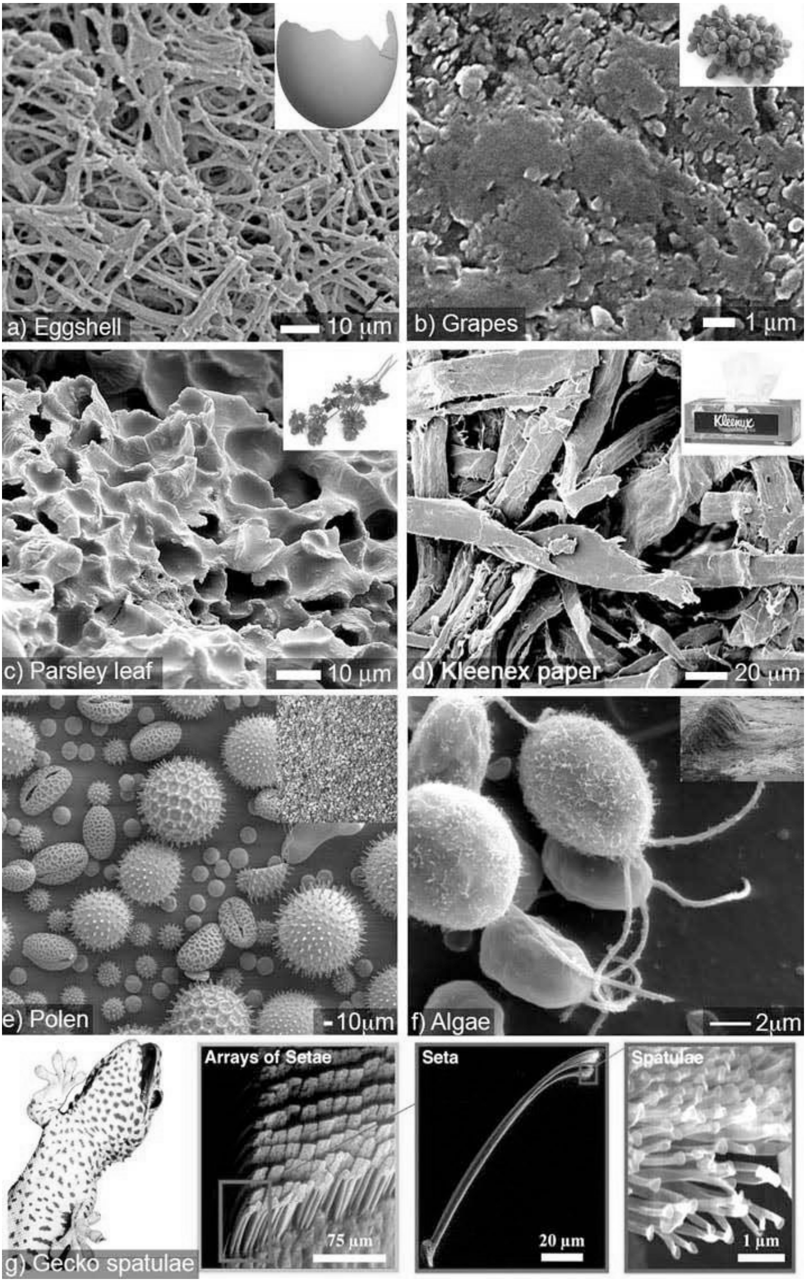
1.3. Nanoparticle composition

1.4. Nanoparticle uniformity and agglomeration

1.1 Dimensionality

As a shape or morphology, nanoparticles play an important role in their therapeutic applications. Based on their number of dimensions, can be divided into 1D, 2D and 3D.

Fig. 1.1 (next page) SEM images showing the complexity of the world at the micro and nanoscale: (a) the inner surface of a bird's eggshell, credit: Janice Carr, Sandra L. Westmoreland, courtesy Public Health Image Library [102]; (b) the rough surface of table grape, credit: Janice Carr, courtesy Public Health Image Library 102]; (c) the textured surface of a parsley leaf, credit: Janice Carr, courtesy Public Health Image Library [102]; (d) Kleenex paper, courtesy of Jim Ekstrom [103]; (e) pollen from a variety of common plants, credit: Louisa Howard, Charles Daghlian, courtesy Public Health Image Library [102];(f) green algae, credit: Elizabeth Smith, Louisa Howard, Erin Dymek, Public Health Image Library [102]; (g) Gecko nano-adhesive system, with increasing magnification from left to right: gecko climbing vertical glass, adhesive surface microstructure, individual setae, nanostructure of spatular endings, courtesy of PNAS [104].


a) Eggshell
10 μm
b) Grapes
1 μm
c) Parsley leaf
10 μm
d) Kleenex paper
20 μm
e) Polen
10μm
f) Algae
2μm
g) Gecko spatulae
Arrays of Setae
75 μm
Seta
20 μm
Spatulae
1 μm

1D nanomaterials:- materials which contain 1 dimension are typically thin films (also known as monolayer thin film) used in computer chips, hard coating on eyeglasses, and in various fields such as electronics, engineering and chemistry.

2D nanomaterials:- materials which contain 2 dimensions in their nanometre scale. Such material includes 2D nanostructure films attached to a substrate or nanopore filters used for the separation and filtration of small particles: e. g. asbestos fibres.

3D nanomaterials:- materials containing all 3 dimensions are considered to be 3D nanomaterials. These include thin films deposited under conditions that generate atomic-scale porosity, colloids, and free nanoparticles with various morphologies.

1.2 Nanoparticle morphology

The morphological characteristics that need to be taken into account are: flatness, sphericity and aspect ratio. Generally classified between high and low aspect ratio particles, high aspect ratio includes nanowires and nanotubes with various shapes like zigzag, belts, helices or diameter (especially nanowires); low aspect ratio includes oval, cubic, prism, helical or pillar, powders, suspension or colloids.

1.3 Nanoparticle composition

Nanoparticles can be composed of a single constituent material or several materials. Mostly commonly found nanoparticles are of agglomerations of materials with various compositions, while pure single constituent materials can be easily synthesized today by a variety of methods.

1.4 Nanoparticle uniformity and agglomeration

According to their chemistry and electro-magnetic characteristics, nanoparticles exist as dispersed aerosols, suspensions/colloids or in an agglomerate state. For example, magnetic nanoparticles form an agglomerate state (cluster) unless their surfaces are coated with non-magnetic materials. Depending upon the size of the agglomerate nanoparticles, these may behave as larger particles.

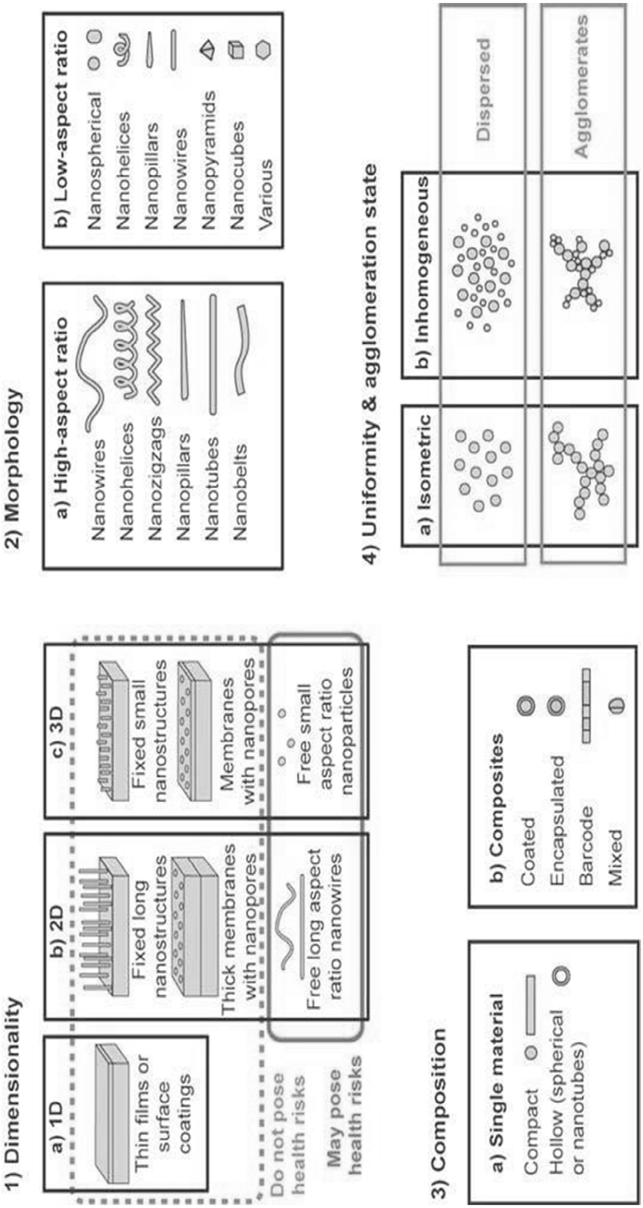


Fig 1.2 Various electro-magnetic characteristics, nanoparticles exist as dispersed aerosols, suspensions/colloids or in an agglomerate state.

Metallic nanoparticles

A term used to describe nanosized metals with dimensions (length, width or thickness) within the size range 1-100 nm. The existence of metallic nanoparticles in solution was first recognized by Faraday in 1857, and a quantitative explanation of their color was given by Mie in 1908.

The main characteristics of metallic nanoparticles

- The large surface energies and larger surface area to volume ratio as compared to the bulk equivalents.
- Provide a specific electronic structure by the transition between a molecular and metallic state.
- Plasmon excitation.
- Quantum confinement.
- Short-range ordering.
- Increased number kinks.
- A large number of low-coordination sites, such as corners and edges, having a large number of “danglingbonds” and, consequently, specific chemical properties, with the ability to store excess electrons.

The prospect of exploiting natural resources for metal nanoparticles synthesis has become a competent and environmentally benign approach [1]. The green synthesis of nanoparticles is an eco-friendly process that can pave the way for researchers across the globe to explore the potential of different herbs in order to synthesize nanoparticles [2].

While there are many conventional methods that have been employed in the syntheses of metal nanoparticles, these contain some serious limitations such as: the generation of hazardous toxic chemicals, the expense, the potential environmental risk, etc., which has encouraged the research scientists to develop more cost-effective, safe, environmentally friendly and eco-friendly approaches to metal nanoparticle synthesis. Thus, *biological* synthesis has increasingly been focused on and promoted as a preferred green principle and process.

Broadly speaking, two methods are employed for the synthesis of metal nanoparticles:

a) **Top-down approach**:- Bulk material is broken down into nanoscale size using different lithographic techniques such as a grinding, milling, stirring, etc.
b) **Bottom-up approach**:- Atoms themselves assemble into new nuclei which grow into a nanoscale particle.

Metal nanoparticles have received considerable attention over recent years owing to their unique properties and practical applications [3, 4]. In recent years, several groups have been reported to have achieved success in the synthesis of Au, Ag and Pd nanoparticles obtained from extracts of plant parts, e.g. leaves [5], lemongrass [6], neem leaves [7-8] and other plants [9]. Researchers have not only been able to synthesize nanoparticles but have also obtained particles with exotic shapes and morphologies [7]. The impressive success in this field has opened-up avenues to develop "greener" methods of synthesizing metal nanoparticles with perfect structural properties using non-toxic starting materials. Traditionally, the chemical and physical methods used to synthesize metal nanoparticles are expensive and often raise questions of environmental risk because they involve the use of toxic, hazardous chemicals [10].

The majority of prevailing synthetic methods are dependent on the use of organic solvents because of the hydrophobicity of the capping agents used [11]. Recently, the search for cleaner methods of synthesis has encouraged the development of bio-inspired approaches. Bio-inspired methods are advantageous compared to other synthetic methods as they are economical and restrict the use of toxic chemicals as well as high pressure, energy and temperatures [12]. Nanoparticles have been found to have diverse applications that may be synthesized by intracellularly or extracellularly, using fungi bacteria, yeast or plant materials. Biogenic nanopartcles are those particles which are synthesized by biogenic systems such as plants, microbes, fish, etc. Nanoparticles are abundant in nature as they are produced by so many natural processes, including volcanic eruption, photochemical reactions by plants, by animals (shedding skin and hair), forest fires (aerosol, ash, etc.), simple erosion, etc. The processes which do not involve harmful or toxic chemicals and solvent systems are referred to as "green synthesis" [Fig. 1.3]. These nanoparticles have been found to possess uniform size, shape and better stability due to the stabilization by proteins and other biomolecules from the biogenic system. Some biogenic systems synthesize these nanoparticles inside the cell, referred to as intracellular biogenic particles; and some are synthesized outside of the cell: referred to as extracellular biogenic particles.

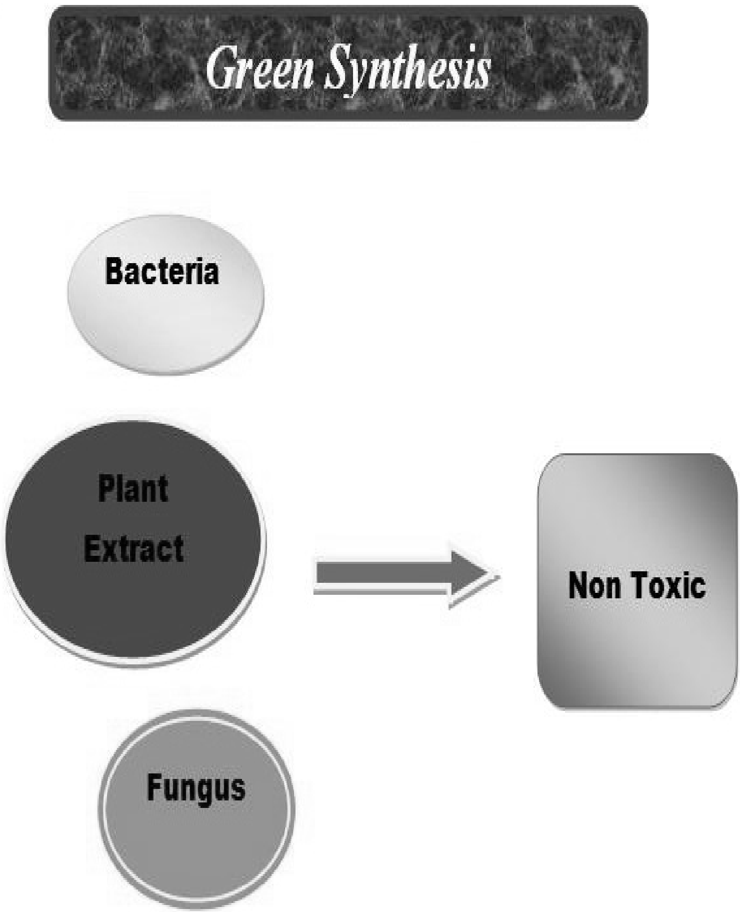


Fig. 1.3 Green Synthesis

The above biological synthesis of metal nanoparticles represents a strategy that is mainly employed to protect the system from the toxic and harsh effects of soluble metal ions, e. g., several plants, and microbes which have a tolerance to toxic ions through this strategy. The most widely synthesized metal nanoparticles are gold and silver, owing to their broad applications in science and technology. "*Mycogenic nanoparticles*" are those which are synthesized using fungal species and "*Bacterioform nanoparticles*" are those which are synthesized by bacterial species.

Even higher plants have been shown to be very effective in synthesizing various metal nanoparticles, having a wide-range of applications in medicinal areas such as antibacterial, anticancer, antifungal, anti-diabetic, anti-aging, etc. Due to their huge variation, plants have been identified as useful for a wide range of applications in the field of pharmaceutics, agriculture, industry, medicine, etc. Interesting reports on plants, and their production of metal nanoparticles, identify numerous advantages, such as: being easily available, very safe to handle, and the widely available biomolecules in plants, such as: tannins, quinines, flavanoids, terpenoids, phenols, alkaloids, colchicines, etc. All are known to mediate the synthesis of metal nanoparticles. Here the biogenic synthesis of palladium, gold and platinum nanoparticles from various different plants by different methods has been the focus of research.

Mechanism for the synthesis of biogenic metal nanoparticles

Different biogenic sources are commonly identified for use in the synthesis of metal nanoparticles, but the mechanism is still not clear. Evidently, plants should act as both a reducing and a stabilizing agent in the synthesis responsible for the formation of metal nanoparticles, stabilizing it for three to four months. The nature of the reducing and stabilizing agent varies according to plant type or the different sources used for the synthesis. Mostly, proteins, peptides, amino acids, polyols and heterocyclic compounds play an important role in the synthesis of metal nanoparticles. Different plants have different properties that are, in turn, responsible for different applications. The properties in question include: amino acids, peptide bond containing amino group, alcohol, acidic group, guanine, indole group, pyroline, sulphur, etc. In other words, every plant has a special characteristic that determines how it is used.

Several amino acids have been implicated in the reduction and stabilization of metal nanoparticles, including: arginine, cysteine, lysine, tryptophan, tyrosine and lysine. Tyrosine residue reduces silver and gold ions under alkaline conditions.

Peptide plays an important role as a reducing agent, as well as a stabilizing agent in many plants. Some investigations have reported that a single amino acid might not be effective as a polypeptide sequence residue. In the synthesis of metal nanoparticles metal ions are reduced to form metal nanoparticles and, for the further promotion of metal nanoparticle formation, they act as a nucleus. Peptides are absorbed into the surface of the metal nanoparticle cluster, which facilitates the reducing environment to reduce more and more metal ions. This process occurs at the interface between the peptide and the metal nuclei and, as a result, nanoparticles of very different sizes are formed.

The advantages of metal nanoparticles are as follows:

- In the body they protect drugs from degrading before they reach their target.
- By preventing drugs from interacting with normal cells, they avoid serious side-effects.
- In the body cells or tissues they control the over-timing and distribution of drugs.
- They increase the absorption of drugs into cancerous cells and tumors.

After the formation of nanoparticles they are characterized by scanning electron microscopy (SEM), UV–visible spectroscopy (UV–vis), dynamic light scattering (DLS), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transformations infrared spectroscopic (FTIR), energy-dispersive X-ray spectroscopy (EDX), etc. This review describes the introduction of the various methods used for the biological synthesis of gold, palladium and platinum nanoparticles, and some of its applications.

Gold

Properties	**Gold**
Discovery and First isolation	In the middle (before **6000 BCE**)
Group and Block	Group 11, d-block
Electronic Configuration	[Xe] $4f^{14}$ $5d^{10}$ $6s^{1}$
Classification	Transition metal
Standard state	Solid
Atomic number	46
Color/for	Metallic yellow, malleable, ductile
Odor	Odorless
Crystal structure	Face centered cubic (fcc)
Melting point (°C)	1064.18
Boiling point (°C)	2970

Table 1.1 Properties of gold nanoparticles.

Gold nanoparticles interact with visible light and produce vibrant colors, for this reason they have been utilized by scientists for centuries. For tracking purposes, spherical nanoparticles can serve as biological tags. In stained-glass windows, gold appears as a red color due to its colloidal nature, something that is applicable to the ultrasensitive and selective detection scheme for DNA. Moreover, it has been discovered that gold nanoparticles contain optical electronic properties that are tunable by changing size, shape, surface chemistry or aggregation state. That is why they have applications in high technology fields such as: organic photovoltaics, as therapeutic agents, electronic conductors, catalysis, in sensor probes, and drug delivery in biological and medicinal applications.

Plants, by also trapping the bio-chemical materials within their parts, use the same nutritive materials for metabolic processes [13]. Using biological organisms such as micro-organisms [14], plant extract or plant biomass could be an alternative to chemical and physical methods for the production of nanoparticles [15, 16]: the plant has many hidden medical benefits [17]. The reduction of gold ions into gold nanoparticles is a time-consuming process. In early studies of the synthesis of gold nanoparticles using micro-organisms, the time required ranged from 2 to 120 hrs [18-20, 14]. The use of microwave radiation nanoparticles synthesis has benefits in that it provides a uniform heating of aqueous solutions and prevents the particles from aggregation [21].

Gold is a well known biocompatible metal; colloidal gold was used as a drinkable solution that exhibited curative properties for several diseases in ancient times [22]. Au nanoparticles have a great bactericidal effect on a wide range of micro-organisms; its bactericidal effect dependent on the size and shape of the particles [23]. In some recent research it is reported that an alga is being used as a biofactory for the synthesis of metallic nanoparticles [24]. Gold nanoparticles have a wide range of applications in nano-scale devices and technologies due to their chemical inertness and resistance to surface oxidation [25].

Gold nanoparticles play a vital role in nanobiotechnology as biomedicine because of their convenient surface bioconjugation with bio molecular probes and remarkable plasmonresonant optical properties [26-28]. Many research articles have reported on the synthesis of gold nanoparticles using plant extracts such as *Ficus religosa* [29], *Memecylon umbellatum* [30], *Macrotiloma uniflorum* [31], *Brevibacterium casei* [32, 33], *Citrus limon, Citrus reticulate* and *Citrus sinensis* [34], *Piper pedicellatum* [35], *Terminalia chebula* [36], and *Banana peel* [37]. Gold nanoparticles have an important function in the delivery of nucleic acids, proteins, gene therapy, *in vivo* delivery, targeting, etc [38]. Some notable works in this field include the use of extracts of Azadirachta indica [39], Cymbopagon flexuosus [40], Cinnamomum camphora [41], Emblica officinalis [42] and Zingiber officinale [43]. Using egg white, fluorescent gold nanoparticles synthesized, egg yolk and sera both play a role as a reducing agent as well as a stabilizing agent. *In vitro* and *in vivo* tumor imaging has shown it can efficiently track cancer cells with excellent biocompatibility [44].

In the biological synthesis of Gold nanoparticles the primary step is the reduction of gold ion (Au^{+3}) to neutral state gold atom (Au^0) which is due to the reduction of chloroauric acid (H $[AuCl_4]$) solution in the presence of a suitable reducing agent. Synthetic reagents are not used as reducing agents due to chemicals being left un-reacted in the reaction, which can be harmful or hazardous. But plants themselves exist as excellent natural compounds that can act as reducing agents as well as stabilizing agents, so that gold nanoparticles, synthesized using plants, do not require a reducing or stabilizing agent. Two important medicinal plants *Cucurbita pepo* and *Malva crispawere* also submitted for synthesis with gold nanoparticles showed that the minimum inhibitory concentration of synthesized gold nanoparticles at 400 μg/ml concentration designating effective inhibitory activity against food spoilage pathogens *Escherichia coli* and *Listeria monocytogenes* [45]. Aqueous leaves extract of *Azadirachta indica*, as a novel source of bio-reductants, were used for the synthesis of gold nanoparticles exhibiting strong cytotoxic effects against MDA-MB-231 cells, suggesting that biologically synthesized gold nanoparticles might be used as new anticancer agents for the treatment of breast cancer [46]. At ambient temperature and pressure, the rate of reduction of metal ions using plant agents is found to be much faster [47].

A rapid formation of gold nanoparticles over a short duration using Sargassum wightii has been achieved by Singaravelu et al. Transmission electron microscopy results showed the formation of well-dispersed gold nanoparticles with a particle size in the range of 8-12 nm [48]. In another study, marine bacteria are exploited to determine their capability in the production of gold nanoparticles. The stable, monodisperse gold nanoparticles of 10 nm size were formed upon exposure to $HAuCl_4$ [49]. Spherical shaped gold nanoparticles with sizes ranging from 10 to 20 nm were synthesized by using Rhodopseudomonas capsulata with a network structure [50]. The small size gold nanoparticles were obtained at lower pH (2.0) in comparison to higher pH (6.0, 7.0) using Escherichia coli and Desulfo vibrio desulfuri can provided with H_2 as the electron donor [51].

The extracellular synthesis of gold nanoparticles, by making use of Pseudomonas fluorescence, has been reported where the nanoparticle size ranged from 50-70 nm [52]. *Cerasus serrulata* leaves extract was used to biosynthesize spherical shaped gold nanoparticles with an approximate size in the range of 5–25 nm, having antibacterial activity against Gram negative (*Escherichia coli*) and Gram positive (*Staphylococcus aureus*) bacteria [53]. Such a method for synthesizing nanoparticles will be an added advantage, and points to other food waste materials that might offer new ways to explore available food compounds for synthesizing gold nanoparticles using green nanotechnology [54].

The mechanism of gold nanoparticles synthesis is still unknown; the different chemical entities present in biogenic compounds may act as reducing agents, reacting with metal ions, leading to their reduction and thereby the synthesis of metal nanoparticles [55].

Temperature plays an important role in reaction, something that controls the aspect ratio and relative amounts of gold nanoparticles shaped like triangles and spheres. Most gold ions first form nuclei, and the secondary growth of the particles stops at higher temperatures because the reaction rate is very high [56]. The effect of different reaction parameters, such as pH, metal ion concentration, time of reaction, and the percentage of extract on the formation of silver and gold nanoparticles has been investigated [57].

Temperature variations in reaction conditions result in the fine tuning of the shape, size and optical properties of the anisotropic nanoparticles [58]. The size of gold nanoparticles was shown to increase at higher reaction temperatures as explained by an increase in the fusion efficiency of micelles, which dissipates supersaturation [59]. The spherical and hexagonal gold nanopartcles of size $\sim$20 nm using Hovenia dulcis extract were synthesized and their *in vitro* antioxidant and antibacterial properties were investigated, which were found to be significant [60]. Ionic forms of gold were shown to have cytotoxicity on various cell types and an adverse effect on red blood cells [61].

Gold nanoparticles are widely used in biomedicine such as tissue, tumor engineering, drug delivery and delivery of DNA vaccine using gene gun gold nanoparticles [62, 63, 64]. Gold nanoparticles also possess important activities like anticoagulant activity, cancer therapy, antimicrobial, etc. Compared to conventional chemical methods, biologically synthesized gold nanoparticles are free from toxic materials and can be used in various applications.

Biologically synthesized gold nanoparticles have several advantages, such as being: single step, eco-friendly, cost effective and having a biocompatible nature. Biogenic components themselves act as both a stabilizing and reducing agent, while also acting as a capping agent. Consequently, the biological method does not need to add any external reducing agent or stabilizing agent, thus reducing the time necessary for synthesis compared to chemical synthesis. Another advantage of biologically synthesis is that it can reduce the number of steps in the process, including the attachment of some functional groups to the gold nanoparticles surface, making them biologically active, an additional step that is required in chemical synthesis [65].

Palladium

Properties	Palladium
Discovery and First isolation	William Hyde Wollaston (1803)
Group and Block	Group 10, d-block
Electronic Configuration	[Kr] $5d^{10}$
Classification	Transition metal
Standard state	Solid
Atomic number	46
Color/for	Silvery-white, ductile metal, malleable
Odour	Odorless
Crystal structure	Face centered cubic (fcc)
Melting point (°C)	1554.9
Boiling point (°C)	2963

Table 1.2 Properties of palladium nanoparticles.

Palladium is a steel white, ductile metal, occurring alongside other platinum group metals and nickel, but in very low concentrations (<1 µg/kg) within the earth’s crust. It has three oxidation states: Pd^0, Pd^{+2} and Pd^{+4}. Among these three states, palladium mainly possesses Pd^{+2} and Pd^0, states that are metallic in nature. Palladium metal shows a resistance to attack by most of the reagents, but not to aqua regia and nitric acid. Moreover, it is stable in air. Palladium has been found in plant ash, which suggests that it is more environmentally mobile and, thus, more easily bioavailable to plants than is the case with platinum.

Palladium possesses excellent hydrogenation and dehydrogenation catalyst properties in organo metallic reactions; as such, it has been found to be a very effective catalyst in a variety of chemical reactions due to its large surface area.

Among various metallic nanoparticles, palladium nanoparticles possess many unique applications, there being many fundamental and conventional methods which are described in the literature for the synthesis of palladium nanoparticles. In most of the cases the Pd NPs were synthesized by chemical, electrochemical or sonochemical methods, using dendrimers, polymers, or metal-organic frameworks as stabilizers [66-68]. Especially, stable colloidal Pd NPs, supported by conventional and non-conventional supports, have been exploited as catalysts for Suzuki cross coupling reactions [69-71]. Among the metallic NPs, Pd has a variety of applications in the field of both homogeneous and heterogeneous catalysis [72-74]. Various catalytic reactions explored using Pd NPs include hydrogenations, oxidations, carbon–carbon coupling as well as electrochemical reactions [75-78].

At present, there are several chemical and biological methods available for the production of metallic nanoparticles such as gold, silver, palladium, copper and platinum. Palladium nanoparticles are mostly used in industries playing a catalytic role and also in biological systems. In addition, there are some bio mimetic approaches that have been reported for the preparation of palladium nanoparticles. For this reason, and given that palladium nanoparticles are widely used on human contacting areas, there is a need for environmentally-friendly green methods for the synthesis of palladium nanoparticles, methods which do not contain any harmful or toxic chemicals. In this domain, then, green methods for the synthesis of palladium nanoparticles are very convenient, easy to use, and eco-friendly.

Although, there are some reports on the green synthesis of Pd NPs using plant materials, e.g., extracts of banana peel, leaf extracts of soya bean and Anacardium occidentale, broth of Cinnamomum camphora leaf, bark of Cinnamom zeylanicum and tuber of Curcuma longa as bioreductants, but they are not as extensive as those published for gold and silver NPs [79-84]. Plant extracts represent a rich source of flavonoids, polyphenols, amides, terpenoids, amino acids and proteins.

Platinum

Properties	Platinum
Discovery and First isolation	Antonio de Ulloa (1748)
Group and Block	Group 10, d-block
Electronic Configuration	[Xe] $4f^{14}$ $5d^{9}$ $6s^{1}$
Classification	Transition metal
Standard state	Solid
Atomic number	78
Color/for	Silvery-white, ductile metal, malleable
Odour	Odorless
Crystal structure	Face centered cubic (fcc)
Melting point (°C)	1768.3
Boiling point (°C)	3825

Table 1.3 Properties of platinum nanoparticles.

Platinum is one of the most precious, rare and expensive metals. It plays a catalytic role in automotive catalytic converters and petrochemical cracking, it also has high corrosion resistance. Platinum nanoparticles are basically used in the form of colloid or suspension in a fluid. Due to its antioxidant properties it has become of one of the most extensively researched subjects.

Noble metal nanoparticles such as silver, gold and platinum are widely used in several products like shampoo, soap, shoes, toothpaste, detergents, cosmetics, and also in the pharmaceutical and medical area. As can be seen then, platinum often comes into direct contact with the human body. The well-known platinum compound, cis-platin (cis-diaminedichloroplatinum), has been used as an anti-tumor agent [85]. Platinum nanoparticles have been used in biomedical applications in combination with the nanoparticles of other metals: in alloy, core-shell, or bimetallic nanocluster form [85]. Yolk shell nanocrystals of FePt@CoS2 have been found to be more potent in killing HeLa cells as compared to cis-platin [86]. There is a growing need to develop processes with important applications for the synthesis of metal nanoparticles that are environmentally-friendly and non-toxic to the human body.

In the literature only a few reports have looked at the synthesis of platinum nanoparticles by biological methods. Biological methods for nanoparticle synthesis using micro-organisms, enzymes, and plants or plant extracts have been suggested as possible eco-friendly alternatives to chemical and physical methods [87, 88]. Biosorption of platinum by the sulfate-reducing bacterium Desulfovibrio desulfuricans has been reported [89]. It has also been found that resting cells of Shewanella algae reduced aqueous $PtCl_6^{2-}$ into elemental platinum within 60 mins at room temperature and neutral pH conditions when lactate was provided as an electron donor [90]. Some of the factors that are responsible for the size of the nanoparticle are: temperature, reaction conditions and also the ratio of plant extract and $PtCl_6$ solution.

The formation of metal nanoparticles has often been effected by stability issues in aqueous solutions that have resulted in particle aggregation due to van der Waal's forces of attraction [91, 92]. For this reason a number of synthetic additives or "capping agents," such as polyvinylpyrrolidone (PVP) [93, 94] or sodium polyacrylate [95], have been reported to absorb the surface of the nanoparticle, thereby not only sterically stabilizing them and preventing this aggregation, but allowing the additional advantage of morphology control [94, 96]. There have been, however, a number of disadvantages in the use of these synthetic stabilizers, including the total inhibition of particle growth if bound too tightly [97], particle deformation [98] and reduced catalytic activity [99]. For these reasons, more natural routes have been explored, where biological molecules such as DNA [100], proteins (bovine serum albumen) and amino acids (l-cysteine) were exploited to the same effect, negating the need for synthetic polymers [91].

References

1. Bhattacharya, Debaditya, and Rajinder K. Gupta. "Nanotechnology and potential of microorganisms." *Critical reviews in biotechnology* 25, no. 4 (2005): 199-204.
2. Savithramma, N., M. Linga Rao, and P. Suvarnalatha Devi. "Evaluation of antibacterial efficacy of biologically synthesized silver nanoparticles using stem barks of Boswellia ovalifoliolata Bal. and Henry and Shorea tumbuggaia Roxb." *Journal of biological sciences* 11, no. 1 (2011): 39-45.
3. Ahmad, Absar, Priyabrata Mukherjee, Satyajyoti Senapati, Deendayal Mandal, M. Islam Khan, Rajiv Kumar, and Murali Sastry. "Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium oxysporum." *Colloids and surfaces B: Biointerfaces* 28, no. 4 (2003): 313-318.

4. Shahverdi, Ahmad R., Sara Minaeian, Hamid Reza Shahverdi, Hossein Jamalifar, and Ashraf-Asadat Nohi. "Rapid synthesis of silver nanoparticles using culture supernatants of Enterobacteria: a novel biological approach." *Process Biochemistry* 42, no. 5 (2007): 919923.
5. Shankar, S. Shiv, Absar Ahmad, and Murali Sastry. "Geranium leaf assisted biosynthesis of silver nanoparticles." *Biotechnology progress* 19, no. 6 (2003): 1627-1631.
6. Shankar SS, Rai A, Ahmad A, Sastry M.," Rapid synthesis of Au, Ag, and bimetallic Au coreAg shell nanoparticles using Neem (Azadirachta indica) leaf broth." *J Colloid Interface Sci.* 275 no. 2 (2004): 496-502.
7. Shankar, S. Shiv, Akhilesh Rai, Absar Ahmad, and Murali Sastry. "Controlling the optical properties of lemongrass extract synthesized gold nanotriangles and potential application in infrared-absorbing optical coatings." *Chemistry of Materials* 17, no. 3 (2005): 566-572.
8. Chandran, S. Prathap, Minakshi Chaudhary, Renu Pasricha, Absar Ahmad, and Murali Sastry. "Synthesis of gold nanotriangles and silver nanoparticles using Aloevera plant extract." *Biotechnology progress* 22, no. 2 (2006): 577-583.
9. Huang, Jiale, Qingbiao Li, Daohua Sun, Yinghua Lu, Yuanbo Su, Xin Yang, Huixuan Wang et al. "Biosynthesis of silver and gold nanoparticles by novel sundried Cinnamomum camphora leaf." *Nanotechnology* 18, no. 10 (2007): 105104.
10. Tripathy, A., Ashok M. Raichur, N. Chandrasekaran, T. C. Prathna, and Amitava Mukherjee. "Process variables in biomimetic synthesis of silver nanoparticles by aqueous extract of Azadirachta indica (Neem) leaves." *Journal of Nanoparticle Research* 12, no. 1 (2010): 237246.
11. Raveendran, Poovathinthodiyil, Jie Fu, and Scott L. Wallen. "Completely "green" synthesis and stabilization of metal nanoparticles." *Journal of the American Chemical Society* 125, no. 46 (2003): 13940-13941.
12. Parashar, Upendra Kumar, Preeti S. Saxena, and Anchal Srivastava. "Bioinspired synthesis of silver nanoparticles." *Digest Journal of Nanomaterials & Biostructures (DJNB)* 4, no. 1 (2009).
13. Gnanajobitha, Gnanadhas, Kanniah Paulkumar, Mahendran Vanaja, Shanmugam Rajeshkumar, Chelladurai Malarkodi, Gurusamy Annadurai, and Cellapandian Kannan. "Fruitmediated synthesis of silver nanoparticles using Vitis vinifera and evaluation of their

antimicrobial efficacy." *Journal of Nanostructure in Chemistry* 3, no. 1 (2013): 67

14. Malarkodi, Chelladurai, Shunmugam Rajeshkumar, Kanniah Paulkumar, Mahendran Vanaja, Gnana Dhas Gnana Jobitha, and Gurusamy Annadurai. "Bactericidal activity of bio mediated silver nanoparticles synthesized by Serratia nematodiphila." *Drug Invention Today* 5, no. 2 (2013): 119-125.
15. Vanaja, M., S. Rajeshkumar, K. Paulkumar, G. Gnanajobitha, C. Malarkodi, and G. Annadurai. "Kinetic study on green synthesis of silver nanoparticles using Coleus aromaticus leaf extract." *Adv. Appl. Sci. Res* 4, no. 3 (2013): 50-55.
16. Gnanajobitha, G., S. Rajeshkumar, C. Kannan, and G. Annadurai. "Preparation and characterization of fruit-mediated silver nanoparticles using pomegranate extract and assessment of its antimicrobial activity." *J. Environ. Nanotechnol* 2, no. 1 (2013): 04-10.
17. Sachdewa, A. R. C. H. A. N. A., and L. D. Khemani. "A preliminary investigation of the possible hypoglycemic activity of Hibiscus rosa-sinensis." *Biomedical and environmental sciences: BES* 12, no. 3 (1999): 222-226.
18. Rajeshkumar, Shanmugam, Chellapandian Kannan, and Gurusamy Annadurai. "Green synthesis of silver nanoparticles using marine brown algae Turbinaria conoides and its antibacterial activity." *International Journal of Pharma and Bio Sciences* 3, no. 4 (2012): 502510.
19. Husseiny, M. I., M. Abd El-Aziz, Y. Badr, and M. A. Mahmoud. "Biosynthesis of gold nanoparticles using Pseudomonas aeruginosa." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 67, no. 3 (2007): 1003-1006.
20. Mukherjee, Priyabrata, Satyajyoti Senapati, Deendayal Mandal, Absar Ahmad, M. Islam Khan, Rajiv Kumar, and Murali Sastry. "Extracellular synthesis of gold nanoparticles by the fungus Fusarium oxysporum." *ChemBioChem* 3, no. 5 (2002): 461-463.
21. Saifuddin, N., C. W. Wong, and A. A. Yasumira. "Rapid biosynthesis of silver nanoparticles using culture supernatant of bacteria with microwave irradiation." *Journal of Chemistry* 6, no. 1 (2009): 61-70.
22. Daniel, Marie-Christine, and Didier Astruc. "Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology." *Chemical reviews* 104, no. 1 (2004): 293-346.

23. Dror-Ehre, A., H. Mamane, T. Belenkova, G. Markovich, and A. Adin. "Silver nanoparticle–E. coli colloidal interaction in water and effect on E. coli survival." *Journal of Colloid and Interface Science* 339, no. 2 (2009): 521-526.
24. De Almeida, Cynthia Layse F., De S. Falcão, De M. Lima, R. Gedson, De A. Montenegro, Narlize S. Lira, Petrônio F. De Athayde-Filho et al. "Bioactivities from marine algae of the genus Gracilaria." *International journal of molecular sciences* 12, no. 7 (2011): 4550-4573.
25. Sugunan, A., C. Thanachayanont, Joydeep Dutta, and J. G. Hilborn. "Heavy-metal ion sensors using chitosan-capped gold nanoparticles." *Science and Technology of Advanced Materials* 6, no. 3 (2005): 335-340.
26. Daniel, Marie-Christine, and Didier Astruc. "Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology." *Chemical reviews* 104, no. 1 (2004): 293-346.
27. Wu, Chien-Chen, and Dong-Hwang Chen. "Facile green synthesis of gold nanoparticles with gum arabic as a stabilizing agent and reducing agent." *Gold Bulletin* 43, no. 4 (2010): 234240.
28. Kreibig, Uwe, and Michael Vollmer. "Theoretical considerations." In *Optical Properties of Metal Clusters*, pp. 13-201. Springer Berlin Heidelberg, 1995.
29. Kirtee Wani, Amit Choudhari, Rajeev Chikate and Ruchika Kaul-Ghanekar 'Synthesis and characterization of gold nanoparticles using Ficus religiosa extract. " Carbon – Sci. Tech. 5 no. 1 (2013): 203 – 210.
30. Arunachalam, Kantha D., Sathesh Kumar Annamalai, and Shanmugasundaram Hari. "Onestep green synthesis and characterization of leaf extract-mediated biocompatible silver and gold nanoparticles from Memecylon umbellatum." *Int J Nanomedicine* 8 (2013): 1307-1315.
31. Aromal, S.A., V.K. Vidhu and D. Philip, pectrocim Acta A mol. Biomol spectosc, 85(1), (2012), 99-104.
32. Kalishwaralal, Kalimuthu, Venkataraman Deepak, SureshBabu Ram Kumar Pandian, Muniasamy Kottaisamy, Selvaraj BarathManiKanth, Bose Kartikeyan, and Sangiliyandi Gurunathan. "Biosynthesis of silver and gold nanoparticles using Brevibacterium casei." *Colloids and Surfaces B: Biointerfaces* 77, no. 2 (2010): 257-262.

33. Mittal, Amit Kumar, Yusuf Chisti, and Uttam Chand Banerjee. "Synthesis of metallic nanoparticles using plant extracts." *Biotechnology advances* 31, no. 2 (2013): 346-356.
34. Sujitha, Mohanan V., and Soundarapandian Kannan. "Green synthesis of gold nanoparticles using Citrus fruits (Citrus limon, Citrus reticulata and Citrus sinensis) aqueous extract and its characterization." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 102 (2013): 15-23.
35. Tamuly, C., M.M. Hazarika, SCh Borah, M.R. Das and M.P.Boruah,.” In situ biosynthesis of Ag, Au and bimetallic nanoparticles using Piper pedicellatum C.D.C., greenchemistry approach.” *Colloids Surf B Biointerfaces*. 1, no. 102 (2013): 627-34.
36. Kumar, Kesarla Mohan, Badal Kumar Mandal, Madhulika Sinha, and Varadhan Krishnakumar. "Terminalia chebula mediated green and rapid synthesis of gold nanoparticles." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 86 (2012): 490-494.
37. Bankar, A.B.Joshi, A.R.Kumar and S.Zinjarde, colloids Surf B Biointerfaces, 1.80(1), (2010), 45-50.
38. Tiwari, Pooja M., Komal Vig, Vida A. Dennis, and Shree R. Singh. "Functionalized gold nanoparticles and their biomedical applications." *Nanomaterials* 1, no. 1 (2011): 31-63.
39. Anuradha, J., Tasneem Abbasi, and S. A. Abbasi. "'Green'synthesis of gold nanoparticles with aqueous extracts of neem (Azadirachta indica)." *Research Journal of Biotechnology* 5, no. 1 (2010): 75-79.
40. Shankar, S. Shiv, Akhilesh Rai, Absar Ahmad, and Murali Sastry. "Controlling the optical properties of lemongrass extract synthesized gold nanotriangles and potential application in infrared-absorbing optical coatings." *Chemistry of Materials* 17, no. 3 (2005): 566-572.
41. Huang, Jiale, Qingbiao Li, Daohua Sun, Yinghua Lu, Yuanbo Su, Xin Yang, Huixuan Wang et al. "Biosynthesis of silver and gold nanoparticles by novel sundried Cinnamomum camphora leaf." *Nanotechnology* 18, no. 1 (2007): 105104.
42. Ankamwar, Balaprasad, Chinmay Damle, Absar Ahmad, and Murali Sastry. "Biosynthesis of gold and silver nanoparticles using Emblica officinalis fruit extract, their phase transfer and transmetallation in an organic solution." *Journal of nanoscience and nanotechnology* 5, no. 10 (2005): 1665-1671.

43. Kumar, K. Praveen, Willi Paul, and Chandra P. Sharma. "Green synthesis of gold nanoparticles with Zingiber officinale extract: characterization and blood compatibility." *Process Biochemistry* 46, no. 10 (2011): 2007-2013.
44. Li, Linlin, Xi Liu, Changhui Fu, Longfei Tan, and Huiyu Liu. "Biosynthesis of fluorescent gold nanoclusters for *in vitro* and *in vivo* tumor imaging." *Optics Communications* 355 (2015): 567574.
45. Chandran, Krishnaraj, Seonhwa Song, and Soon-Il Yun. "Effect of size and shape controlled biogenic synthesis of gold nanoparticles and their mode of interactions against food borne bacterial pathogens." *Arabian Journal of Chemistry* (2014).
46. Krishnaraj, C., P. Muthukumaran, R. Ramachandran, M. D. Balakumaran, and P. T. Kalaichelvan. "Acalypha indica Linn: biogenic synthesis of silver and gold nanoparticles and their cytotoxic effects against MDA-MB-231, human breast cancer cells." *Biotechnology Reports* 4 (2014): 42-49.
47. Bhau, B. S., Sneha Ghosh, Sangeeta Puri, B. Borah, D. K. Sarmah, and Raju Khan. "Green synthesis of gold nanoparticles from the leaf extract of Nepenthes khasiana and antimicrobial assay." *Adv Mater Lett* 6, no. 1 (2015): 55-58.
48. Singaravelu, G., J. S. Arockiamary, V. Ganesh Kumar, and K. Govindaraju. "A novel extracellular synthesis of monodisperse gold nanoparticles using marine alga, Sargassum wightii Greville." *Colloids and Surfaces B: Biointerfaces* 57, no. 1 (2007): 97-101.
49. Sharma, Nishat, Anil K. Pinnaka, Manoj Raje, F. N. U. Ashish, Mani Shankar Bhattacharyya, and Anirban Roy Choudhury. "Exploitation of marine bacteria for production of gold nanoparticles." *Microbial cell factories* 11, no. 1 (2012): 86.
50. He, Shiying, Yu Zhang, Zhirui Guo, and Ning Gu. "Biological synthesis of gold nanowires using extract of Rhodopseudomonas capsulata." *Biotechnology Progress* 24, no. 2 (2008): 476-480.
51. Deplanche, K., and L. E. Macaskie. "Biorecovery of gold by Escherichia coli and Desulfovibrio desulfuricans." *Biotechnology and bioengineering* 99, no. 5 (2008): 1055-1064.
52. Rajasree, SR Radhika, and T. Y. Suman. "Extracellular biosynthesis of gold nanoparticles using a Gram negative bacterium Pseudomonas fluorescens." *Asian Pacific Journal of Tropical Disease* 2 (2012): S796-S799.
53. Karthik, R., Shen-Ming Chen, A. Elangovan, P. Muthukrishnan, R. Shanmugam, and BihShow Lou. "Phyto mediated biogenic synthesis of gold nanoparticles using Cerasus serrulata and its