

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

*A Review*

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Cambridge  
Scholars  
Publishing



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This book first published 2018

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

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ISBN (10): 1-5275-1178-2

ISBN (13): 978-1-5275-1178-1

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## ACKNOWLEDGEMENTS

It is a great privilege to acknowledge my immense indebtedness to Prof. K.A. Parmar and Prof. C.P. Bhasin, Department of Chemistry for their valuable guidance, suggestions and affection throughout my research work.

I would also like to express my gratitude to the members of our laboratory for their affectionate company and co-operation throughout my research work.

I convey my genuine thanks to Miss Kavita Desai, Miss Bijal Patel, Miss Tessy John, Miss Trupti Kukadiya, Miss Sweety Patel, Mr. Jayesh Jadhav, Mr. Shailesh Vajapara, Dr. Jyotindra Mahayavansi, Mr. Vikram Solanki, Mr. Shailesh Kotval and Mr. Dhaval Prajapati for their key suggestions and cooperation in helping me to form my research framework.

From the bottom of my heart, I express my gratitude to my loving parents, my father Mr. Mahendrabhai Vaghela and my mother Smt. Hansaben M. Vaghela. I truly thank my brothers, Mr. Jigar M. Vaghela and Mr. Akash M. Vaghela who have always supported and encouraged me. I am very thankful for their cherished devotion, love and care.





# CHAPTER ONE

## INTRODUCTION

The prefix “nano” derives from the Greek word “nanos” signifying “dwarf” (one billionth of a meter  $10^{-9}\text{m}$ ), 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

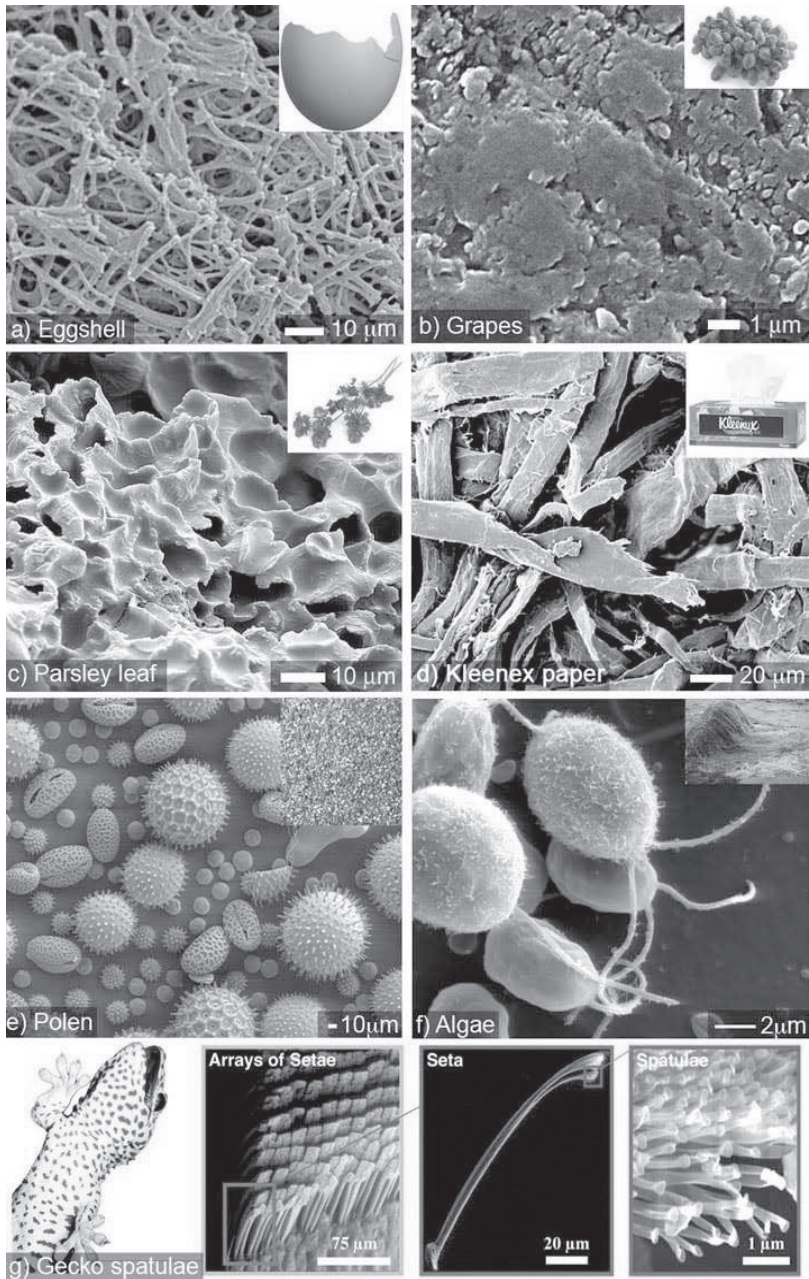
1.3. Nanoparticle composition

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].



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.

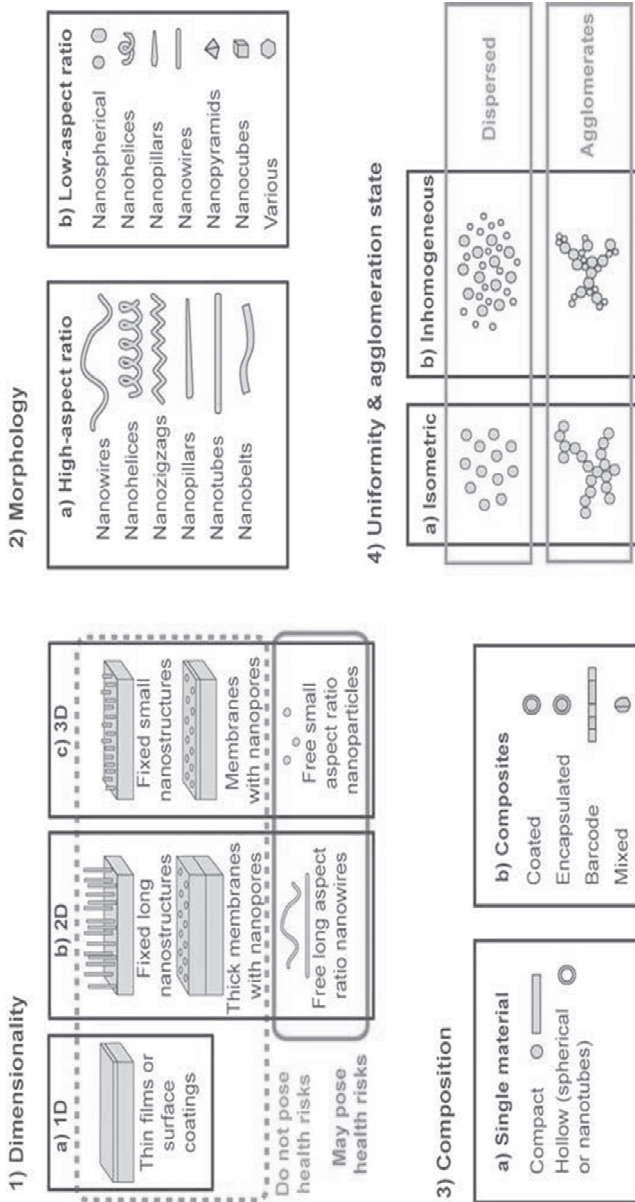


Fig 1.2 Various electro-magnetic characteristics, nanoparticles exist as dispersed aerosols, suspensions/colloids or in an agglomerate state.

## 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 synthesise 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 nanoparticles 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.



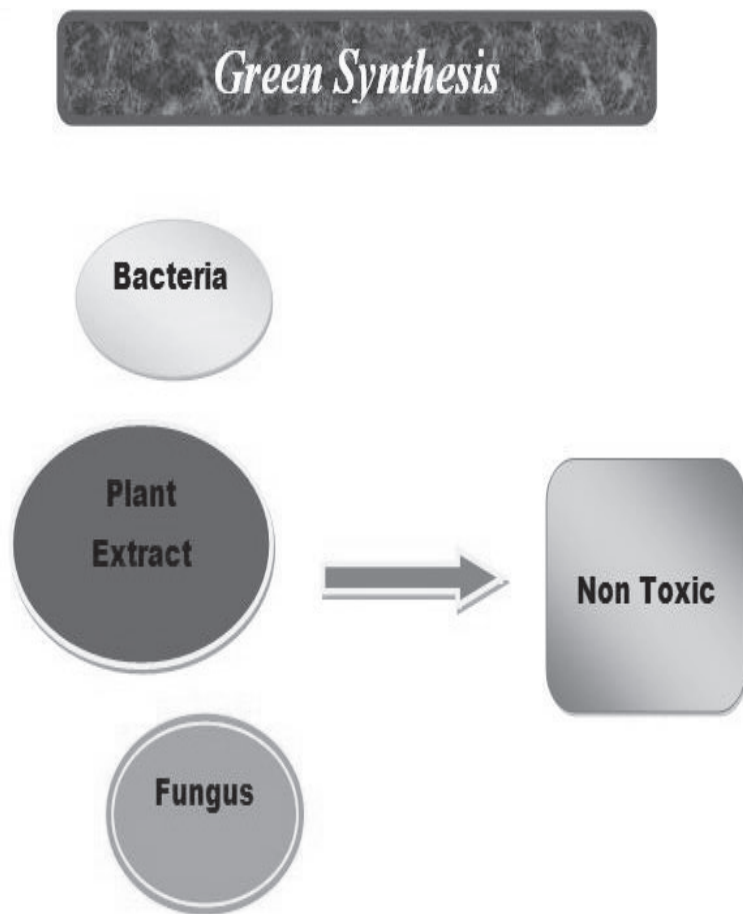


Fig. 1.3 Green Synthesis

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 pharmaceuticals, 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, pyrrole, 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 <b>6000 BCE</b> )
Group and Block	Group 11, d-block
Electronic Configuration	$[\text{Xe}] 4f^{14} 5d^{10} 6s^1$
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 religiosa* [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], *Cymbopogon flexuosus* [40], *Cinnamomum camphora* [41], *Embllica 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  $\mu g/ml$  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 *Rhodospseudomonas 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 fluorescens*, 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 nanoparticles of size ~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 biological 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 <sup>10</sup>
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<sup>0</sup>, Pd<sup>+2</sup> and Pd<sup>+4</sup>. Among these three states, palladium mainly possesses Pd<sup>+2</sup> and Pd<sup>0</sup>, 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 <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>
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 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@CoS<sub>2</sub> 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  $\text{PtCl}_6^{2-}$  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  $\text{PtCl}_6$  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].

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# CHAPTER TWO

## LITERATURE SURVEY

### 1. Gold

Report on: C. Krishnaraj, *Et al.* “*Acalypha indica* linn: biogenic synthesis of silver and gold nanoparticles and their cytotoxic effects against MDA-MB-231, human breast cancer cells.”

This study investigates the *in vitro* cytotoxic effect of biologically synthesized silver and gold nanoparticles on MDA-MB-231, human breast cancer cells. The formation of silver and gold nanoparticles was observed over a 30-minute period and the various characterization techniques such as UV-vis spectrophotometer, FE-SEM, TEM and XRD studies were confirmed by the synthesis of nanoparticles. Further, MTT, acridine orange and ethidium bromide (AO/EB) dual staining, caspase-3 and DNA fragmentation assays were carried out using various concentrations of silver and gold nanoparticles ranging from 1 to 100mg/ml. At 100mg/ml. concentration, the plant extract derived nanoparticles exhibited significant cytotoxic effects and the apoptotic features were confirmed through caspase-3 activation and DNA fragmentation assays. Thus, the results of this study indicate that biologically synthesized silver and gold nanoparticles might be used to treat breast cancer; however, further clinical studies are necessary to ascertain their potential as anticancer agents [1].

Report on: K.S. Uma Suganya, *Et al.* “Blue green alga mediated synthesis of gold nanoparticles and its antibacterial efficacy against gram positive organisms.”

Biofunctionalized gold nanoparticles (AuNPs) play an important role in the design and development of nanomedicine. The synthesis of AuNPs from biogenic materials is environmentally benign and possesses high bacterial inhibition and bactericidal properties. In the present study, blue green alga *Spirulina platensis* protein edited synthesis of AuNPs and its antibacterial activity against Gram positive bacteria is discussed. AuNPs

were characterized using ultraviolet–visible (UV–vis) spectroscopy, fluorescence spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, high resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray analysis (EDAX). Stable, well-defined AuNPs of smaller and uniform shape with an average size of ~5 nm were obtained. The antibacterial efficacy of protein functionalized AuNPs were tested against Gram positive organisms *Bacillus subtilis* and *Staphylococcus aureus* [2].

Report on: Monalisa Pattanayak, *Et al.* “Green synthesis of gold nanoparticles using *Cucumis sativus* (cucumber) aqueous extract.”

The present study explores the reducing and capping potential of aqueous extract from the juice of cucumber for the synthesis of gold nanoparticles. The extract with different concentrations is reduced with HAuCl<sub>4</sub> aqueous solution at room temperature. The color change, pH change and UV-visible spectroscopic analysis reveal the surface plasmon resonance (SPR) of the final reaction product, which confirms the reduction of Au<sup>3+</sup> ion to gold nanoparticles. XRD, particle size analysis results demonstrate the strong reducing potential of cucumber aqueous extract, something that can also be tested in the green synthesis of other metallic nanoparticles [3].

Report on: Monalisa Pattanayak and P.L. Nayak. “Green synthesis of gold nanoparticles using *Elettaria cardamomum* (ELAICHI) aqueous extract.”

The present study explores the reducing and capping potential of aqueous extract from the seed pod of Elaichi for the synthesis of gold nanoparticles. The extract with different concentrations is reduced with HAuCl<sub>4</sub> aqueous solution at room temperature. The color change, pH change and UV-Visible spectroscopic analysis reveal the surface plasmon resonance (SPR) of the final reaction product, which confirms the reduction of Au<sup>3+</sup> ion to gold nanoparticles. XRD, particle size analysis results demonstrate the strong reducing potential of Elaichi aqueous extract, something that can also be tested in the green synthesis of other metallic nanoparticles [4].

Report on: Birendra Kumar Bindhaniand Ashok Kumar Panigrahi. “Green synthesis of gold nanoparticles using neem (*Azadirachta indica* L.) leaf extract and its biomedical applications.”

Eco-friendly green synthesis is one of the promising branches of nanoscience because of its potential application in different biomedical fields. It is an attractive option due to the non-toxic and very low cost of

synthesis. This paper deals with the synthesis of eco-friendly and cost effective gold nanoparticles by using leaf extract of neem (*Azadirachta indica*) as a reducing agent. The SEM image shows that the gold nanoparticles are predominantly spherical in morphology whereas the TEM image shows different shapes such as hexagons, triangles and spheres. DLS results indicated that the particle and dispersity of gold nanoparticles revealed an effective diameter of about 15:1nm and polydispersity index (PDI) 0.643. Thus, this rapid, eco-friendly and economical route can be used to synthesise HAuCl<sub>4</sub> with a wide range of biomedical applications [5].

Report on: Varahalarao Vadlapudi and D.S.V.G.K. Kaladhar. "Review: green synthesis of silver and gold nanoparticles."

Nanotechnology is a field that is mushrooming, making an impact in all spheres of human life. Nanobiotechnology represents an economical alternative for chemical and physical methods of nanoparticles formation. Presently available literature reveals that NP synthesis, using marine plants, microorganisms and algae as sources, has been underexplored and underexploited. The development of green processes for the synthesis of NP is evolving into an important branch of nanotechnology. It has many advantages, such as the ease with which the process can be scaled-up, economic viability, etc. At present, the researchers are looking into the development of cost-effective procedures for producing reproducible, stable and biocompatible AgNPs and AuNPs. Antibiotic resistance is the world's major public healthcare problem; AgNPs and AuNPs particles play a vital role in nanobiotechnology as biomedicine against drug-resistant bacteria [6].

Report on: Anish Rajan, *Et al.* "Studies on catalytic, antioxidant, antibacterial and anticancer activities of biogenic gold nanoparticles."

The biosynthesis of the nanoparticles of precious metals has attracted a surge of interest in recent years. In the present study, phytochemicals present in the Areca catechu nut have been used for the synthesis of gold nanoparticles at 300 K, 373 K and under microwave irradiation of 2450 MHz. The synthesized nanoparticles have been characterized using UV-visible, TEM, XRD, and FTIR techniques. Perpetual changes in synthesis conditions are clearly shown, with appreciable morphological variation. An enhanced formation of monodispersed, spherical gold nanoparticles of size 13.7 nm could be obtained under microwave irradiation. XRD pattern confirms the crystalline nature of the as-synthesized nanoparticles. The



biomolecules involved in the reduction and stabilization of nanoparticles have been identified using FTIR spectra. The catalytic efficiency of the synthesized gold nanoparticles of varying size distributions has been demonstrated through the degradation of the organic pollutants: methylene blue, methyl orange, eosin yellowish and 4-nitrophenol. The observed size-dependent catalytic activity may aid in the rapid elimination of industrial wastes, leading to a greener environment. The potential of the phytosynthesized nanogold in scavenging the harmful radical NO and the stable radical DPPH has been evaluated. In addition to its cytotoxic effect on HeLa cell lines, gold nanospheroids synthesized under microwave irradiation have been observed to exhibit an enhanced activity against a broad spectrum of bacterial pathogens as well [8].

Report on: Anand M, *Et al.* “Green phyto-synthesis of gold nanoparticles using *Achyranthes aspera* linn seed-epicotyls layer extract and its anticancer activity.”

In recent decades the green phyto-process for the synthesis of metal incorporated nanoparticles has evolved into being an imperative branch of nanotechnology. There is here reported a rapid, expedient, and extracellular method for the synthesis of gold nanoparticles (AuNPs) by reducing gold chloride with the help of aqueous seed-epicotyls layer extracts of *Achyranthes aspera* Linn (Amarantheceae). This approach is simple, economical, stable over time, reproducible at room temperature and is synthesized in an eco-friendly mode to obtain a self-assembly of AuNPs. The resulting AuNPs were characterized using ultravioletvisible absorption spectroscopy, scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopic techniques. The anticancer activity of the AuNPs was studied against HeLa (Cervical) cancer cell lines. Reported herein for the first time: *A. aspera* seed-epicotyls assisted synthesis of biogenic AuNPs; the NPs are conspicuously smaller and better faceted compared with those synthesized by *A. aspera* leaf extracts previously reported. Synthesized AuNPs showed potent anticancer activity at 50µg/ml concentration against cervical cancer cell lines [9].

Report on: K. Gopinath, *Et al.* “Green synthesis of gold nanoparticles from fruit extract of *Terminalia arjuna*, for the enhanced seed germination activity of *Gloriosa superb.*”

This study offers an account of the synthesis of spherical gold nanoparticles (Au NPs) using the aqueous fruit extract of *Terminalia arjuna*, which contains tannin, terpenoid, saponins, flavonoids, glycosides

and polyphenolic compounds. The synthesized Au NPs were characterized by UV–visible spectroscopy (UV–vis), Fourier transform infrared (FTIR), X-ray diffraction (XRD), atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), dynamic light scattering (DLS) and zeta potential (ZP) analyses. UV–visible spectra of the fruit extract containing Au NPs showed a surface plasmon resonance peak at 523 nm. FTIR analysis was performed to analyze the biomolecules responsible for the reduction of Au NPs. FTIR analysis clearly showed that Au NPs were capped with plant compounds. The EDX analysis was used to identify the elemental composition of the synthesized Au NPs. The high crystallinity of Au NPs with a face centered cubic phase is evident to XRD patterns. AFM and TEM observations revealed that synthesized Au NPs were of a spherical shape with the range 20–50 nm. DLS measurement revealed that Au NPs were obtained in the average size of 25 nm and it is found to be stable at 21.9 mV through ZP analysis. The synthesized Au NPs were investigated for their antibacterial activity. By contrast, Au NPs did not show any antibacterial activity against Gram positive and Gram negative bacteria. The Au NPs were treated with two different concentrations (500 and 1,000 IM) of *Gloriosa superba* seeds. Au NPs exposure at 1,000 IM concentration has a significant effect on the seed germination rate and the vegetative growth of *G. superba*. This is the first report on Au NPs as a biocompatibility material to enhance the seed yield of this endangered medicinal plant [10].

Report on: Samiran Mondala, *Et al.* “Biogenic synthesis of Ag, Au and bimetallic Au/Ag alloy nanoparticles using aqueous extract of mahogany (*Swietenia mahogani* JACQ.) leaves.”

In this paper we see demonstrated for the first time the superb efficiency of aqueous extract of dried leaves of mahogany (*Swietenia mahogani* JACQ.) in the rapid synthesis of stable monometallic Au and Ag nanoparticles, and also Au/Ag bimetallic alloy nanoparticles having spectacular morphologies. The method used was clean, non-toxic and environment-friendly. When exposed to aqueous mahogany leaf extract, the competitive reduction of Au<sup>III</sup> and Ag<sup>I</sup> ions present simultaneously in the same solution leads to the production of bimetallic Au/Ag alloy nanoparticles. UV–visible spectroscopy was used to monitor the kinetics of nanoparticles formation. UV–visible spectroscopic data and TEM images revealed the formation of bimetallic Au/Ag alloy nanoparticles. Mahogany leaf extract contains various polyhydroxy limonoids that are responsible for the reduction of Au<sup>III</sup> and Ag<sup>I</sup> ions, leading to the formation and stabilization of Au and Ag nanoparticles [11].

Report on: Naznin Ara Beguma, *Et al.* “Biogenic synthesis of Au and Ag nanoparticles using aqueous solutions of Black tea leaf extracts.”

Here is explored the application of three different aqueous solutions derived from Black tea leaf extracts in the synthesis of Au and Ag nanoparticles. The plain tea leaf broth, as well as that containing the ethyl acetate extract of tea leaves, were found to be extremely efficient, leading to a rapid formation of stable nanoparticles of various shapes: spheres, trapezoids, prisms and rods. For a given metal ion precursor, the kinetics of particle synthesis were remarkably similar in these two solutions, as evidenced from their absorption spectroscopy monitored over time. Moreover, they exhibited similar redox behaviour. In contrast, with the other solution, containing the dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) extract of tea leaves, the research failed to detect any nanoparticle generation under similar reaction conditions. The results suggest that the reduction of metal ions and stabilization of the resultant particles in the first two solutions involved the same class of biomolecules. The study identified these biomolecules as the tea polyphenols, including flavonoids, which were present in comparable amounts in both the tea leaf broth and ethyl acetate extract, but absent in the  $\text{CH}_2\text{Cl}_2$  extract of tea leaves. The efficiency of the tea leaf extracts within Au and Ag nanoparticle synthesis was compared with that of a naturally occurring hydroxyl flavonoid, quercetin [12].

Report on: Vineet Kumar and Sudesh Kumar Yadav. “Plant-mediated synthesis of silver and gold nanoparticles and their applications.”

Nanobiotechnology deals with the synthesis of nanostructures using living organisms. Among the uses of living organisms for nanoparticle synthesis, plants have found numerous applications, particularly in metal nanoparticle synthesis. The use of plants for the synthesis of nanoparticles could be advantageous across other environmentally benign biological processes, as this method eliminates the elaborate process of maintaining cell cultures. Biosynthetic processes for nanoparticles would be more useful if nanoparticles were produced extracellularly using plants or their extracts, and in a controlled manner according to their size, dispersity and shape. Plant use can also be scaled-up for the large-scale synthesis of nanoparticles. In light of this, the report reviews the use of plants or their extracts in the synthesis of silver and gold nanoparticles for various human applications [13].

Report on: Jiale Huang, *Et al.* “Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf.”

The synthesis of nanocrystals is in the limelight in modern nanotechnology. The biosynthesis of nanoparticles by plant extracts is currently widely employed. Not only could silver nanoparticles ranging from 55 to 80 nm in size be fabricated, but also triangular or spherical-shaped gold nanoparticles can be easily modulated by reacting the novel sundried biomass of *Cinnamomum camphora* leaf with aqueous silver or gold precursors at ambient temperature. The marked difference of shape control between gold and silver nanoparticles is here attributed to the comparative advantage of protective biomolecules and reductive biomolecules. The polyol components and the water-soluble heterocyclic components were mainly responsible for the reduction of silver ions or chloroaurate ions and the stabilization of the nanoparticles, respectively. The sundried leaf in this work was very suitable for the simple synthesis of nanoparticles [14].

Report on: Nima P and Ganesan V. “Green synthesis of silver and gold nanoparticles using flower bud broth of *Couropita guinensis* aublet.”

Metallic nanoparticles have received considerable attention due to their various sizes and shapes in the green synthesis protocol. This study researches the synthesis of silver and gold nanoparticles using *Couropita guinensis* flower bud broth as a reducing agent in the present study. The UV-Visible (UV-Vis) spectroscopic analysis of silver and gold reaction media reveals that the surface plasmon resonance (SPR) vibrations have absorption maxima at 410 and 535nm respectively. These absorption maxima values correspond to the formation of silver and gold nanoparticles. Fourier transform infrared (FT-IR) spectroscopic analysis explains that biomolecules present in the flower bud broth of *Couropita guinensis* become capping agents and are responsible in the synthesis and stabilization of silver and gold nanoparticles. X-ray diffraction (XRD) analysis shows the particle nature and size. Energy dispersive X-ray (EDX) analysis and scanning electron microscopy (SEM) confirm the significant presence of elemental silver and gold nanoparticles in respective reaction media. The obtained silver nanoparticles were almost spherical in shape. The gold reaction medium shows anisotropic gold nanoparticles in a polydispersed manner [15].

Report on: Geethu Isaac and R. Emilin Renitta. “Brown algae mediated synthesis, characterization of gold nano particles using *Padina pavonica* and their antibacterial activity against human pathogens.”

The development of reliable and eco-friendly metallic nanoparticles is an important step in the field of nanotechnology. In order to achieve this, use of natural sources such as biological systems becomes essential. In the present work, extracellular biosynthesis of gold nanoparticles using *Padina pavonica* was carried out and achieved a rapid formation of gold nanoparticles in a short duration of 24 hrs. The UV–vis spectrum of the aqueous medium containing gold ion peaked at 545.5 nm corresponding to the plasmon absorbance of gold nanoparticles. A particle size analyzer confirmed the size range of nanoparticles from 30100nm. X-ray diffraction (XRD) spectrum of the gold nanoparticles exhibited Bragg reflections corresponding to gold nanoparticles. The TEM and EDX results revealed the spherical morphology of gold nanoparticles and the elemental composition. Fourier transform infrared spectroscopy revealed the possible involvement of reductive groups on the surfaces of nanoparticles. The antimicrobial activity of gold nanoparticles was tested against test organisms *Escherichia coli* and *Bacillus subtilis*. The inhibition zone diameter in *B.subtilis* was found to be 15mm or even less, as in the case of *E.coli*. This environment-friendly method of biological gold nanoparticle synthesis can be potentially applied in various products that directly come into contact with the human body, such as cosmetics, foods, and consumer goods, as well as medical applications [16].

Report on: Ratul Kumar Das, *Et al.* “The synthesis of gold nanoparticles using *Amaranthus spinosus* leaf extract and the study of their optical properties.”

This research investigates the application of a medicinally important plant, *amaranthus spinosus*, in the synthesis of gold nanoparticles (AuNPs). Different concentrations of ethanolic leaf extract of the plant were reacted with the aqueous solution of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  under mild reaction conditions. Synthesis of AuNPs was confirmed from the UV-Vis study of the surface plasmon resonance properties of the colloidal solution. Transmission electron microscopy (TEM) revealed particles as spherical and triangular in shape. X-ray diffraction (XRD) confirmed the crystalline nature of AuNPs with an average size of 10.74 nm as determined by DebyeScherrer’s Equation. Fourier transform infrared (FT-IR) analysis of leaf extract and lyophilized AuNPs showed the presence of various functional groups in diverse phytochemicals. Energy dispersive X-ray

(EDX) of purified AuNPs confirmed the formation of AuNPs and surface absorption of biomolecules. The study further investigated the toxicity of the synthesized AuNPs finding them to be non-toxic to the cancer cell lines and thus usable for biomedical applications [17].

Report on: Priya Tharishini P, *Et al.* “Green synthesis of gold nanoparticles from *Cassia auriculata* leaf aqueous extract and its cytotoxicity effect on *in vitro* cell line.”

A simple method for the synthesis of gold nanoparticles is proposed in this paper. The gold nanoparticles were synthesized in an eco-friendly manner using aqueous leaf extracts of *cassia auriculata* where the extracts function as reducing and stabilizing agents. The synthesized nanoparticles were characterized by UV-VIS, HR TEM, SAED, XRD and EDAX. The stability of the gold nanoparticles was studied by UV-VIS absorption spectroscopy. The characteristic surface plasma peak was centred at 530 nm. The HR TEM image revealed the size of nanoparticles in the range of 20-30 nm. XRD and SAED confirmed the crystalline nature of nanoparticles. The elemental composition and purity of gold nanoparticles was analysed by EDAX. The cytotoxicity of synthesized gold nanoparticles was examined on Vero and HeLa cell lines and was found to be non-toxic and hence acceptable for biomedical applications [18].

Report on: Chandan Tamuly *Et al.* “*Biosynthesis* of Au nanoparticles by *Gymnocladus assamicus* and its catalytic activity.”

The subject of this research is the synthesis of gold (Au) nanoparticles by using *Gymnocladu assamicus* pod extract in an aqueous medium. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis revealed that the Au nanoparticles predominantly formed a planar structure and size range 4.570.23–22.571.24 nm with  $2\theta$  value sat 38.221, 44.381, 64.341, 77.61 and 81.241 for lattice plane. The formation of pure metallic nanoparticles by the reduction of their et al ions is facilitated by reducing biphenolic acids such as gallic acid, protocatechuic acid and kaempferol present in the *G. Assamicus* pod extract. The Au solution shows potential catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol [19].

Report on: J. Das and P. Velusamy. “Catalytic reduction of methylene blue using biogenic gold nanoparticles from *Sesbania grandiflora* L.”

This investigation reports on the synthesis of gold nanoparticles (AuNPs) using leaf extract of *Sesbania grandiflora*. The processes of nucleation and

the growth of AuNPs were followed by monitoring the absorption spectra during the reaction. The UV–vis spectrum of the aqueous medium containing AuNPs showed a peak at around 534 nm. FE-SEM and TEM micrograph analysis of the AuNPs indicated that they were predominantly spherical, well dispersed within 7–34 nm. The synthesized AuNPs are observed to have an excellent catalytic activity on the reduction of methylene blue by *S. grandiflora* extract which is confirmed by the decrease in absorbance maximum values of methylene blue (MB) with respect to time using UV–vis spectrophotometer and is thus identified as an effective catalyst for degrading chemical dyes [20].

Report on: Mingxia Guo, *Et al.* “Controllable biosynthesis of gold nanoparticles from a *Eucommialmoides* bark aqueous extract.”

The present work reports on the green synthesis of gold nanoparticles (AuNPs) by the water extract of *Eucommialmoides* (*E. ulmoides*) bark. The effects of various parameters, such as the concentration of reactants, pH of the reaction mixture, temperature and the time of incubation, were explored during the controlled formation of gold nanoparticles. The characterization through high resolution-transmission electron microscopic (HRTEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) infer that the as-synthesized AuNPs were spherical in shape with a face cubic crystal (FCC) structure. The results from zeta potential and dynamic light scattering (DLS) suggest the good stability and narrow size distribution of the AuNPs. This method for the synthesis of AuNPs is simple, economical, non-toxic and efficient. The as-synthesized AuNPs show excellent catalytic activity for the catalytic reducing decoloration of model compounds of azo-dye: reactive yellow 179 and Congo red [21].

Report on: Kamran Tahira, *Et al.* “*Nerium oleander* leaves extract mediated synthesis of gold nanoparticles and its antioxidant activity.”

The present work describes the reduction of gold ions into gold nanoparticles using *nerium oleander* leaf extract in a one step green synthetic method. The formation of gold nanoparticles was confirmed by UV-vis spectroscopic analysis. The gold nanoparticles were characterized by HRTEM, SEM and were found to be small size (2-10 nm), almost spherical in shape and highly dispersed without any aggregation. The XRD confirmed the crystal structure of gold nanoparticles. An EDX detector was used to determine the elemental composition of material. The types of organic compounds present in the plant leaves were detected by

FT-IR spectral analysis. The gold nanoparticles synthesized by this method were pure and showed good antioxidant activity. The results showed that Nerium oleander leaf extract is very active in the reduction of gold nanoparticles [22].

Report on: F. Arockiya Aarthi Rajathi, et al. “Phytofabrication of gold nanoparticles assisted by leaves of Suaeda monoica and its free radical scavenging property.”

Development of biologically inspired experimental processes for the synthesis of nanoparticles is evolving into an important branch of nanotechnology. This eco-friendly synthesis of inorganic nanoparticle is now a fast-growing research area in this thread of nanotechnology. The present study reports on the Suaeda monoica leaf mediated synthesis of gold nanoparticles by the reduction of gold ions. The formation of gold nanoparticles was confirmed by color changes, from turbid brown to deep purple violet, and a characteristic peak at 535 nm. The morphology and structure of synthesized gold nanoparticles were characterized on scanning electron microscopy (SEM) equipped with a thermo EDAX attachment, transmission electron microscopy (TEM), X-ray diffraction (XRD), (FT-IR), dynamic light scattering (DLS) which reveals that the Au nanoparticles are spherical and the average particle size is 12.96 nm. The crystalline nature of the nanoparticles is confirmed from the XRD pattern. The FTIR spectrum indicates that the biomolecules of carboxyl, amine and hydroxyl functional groups are involved in the reduction of gold nanoparticles. The biosynthesized gold nanoparticles displayed considerable antioxidant capacity [23].

Report on: Sabjan Khaleel Basha, *Et al.* “Phytochemical mediated gold nanoparticles and their PTP 1B inhibitory activity.”

Current research demonstrates the rapid formation of gold nanoparticles with guavanoic acid a phytochemical of Psidium guajava (Pg). The pharmacological capabilities of the phytochemicals present in the leaves of Pg and their ability to generate gold nanoparticles is presented herein. The new genre of green nanoparticles exhibit remarkable protein tyrosine phosphatase 1B (PTP 1B) inhibitory activity and *in vitro* stability in various physiological medium including saline, histidine, cysteine, bovine serum albumin (BSA), human serum albumin (HSA) and buffers (pH 5, 7 and 9). It is predicted that this new technology will have an enormous impact in several domains of the pharmaceutical industry [24].



Report on: Moorthy Ganeshkumar, *Et al.* “Spontaneous ultra fast synthesis of gold nanoparticles using Punica granatum for cancer targeted drug delivery.”

Rapid synthesis of mono-dispersed gold nanoparticles through an economically feasible green chemistry approach is highly desirable. This study develops a method to synthesize mono-dispersed gold nanoparticles (PAuNPs) by mixing gold solution with fruit peel extract of Punica granatum without using any surfactant or external energy. In this method, physiologically stable, biocompatible PAuNPs were formed within 60 s. Casein, being a biocompatible polymer, is used to couple the prepared PAuNPs for the functionalization of folic acid, which is highly expressed in cancer cells. These functionalized PAuNPs could be used for targeted drug delivery for cancer with enhanced therapeutic efficacy and minimal side effects. PAuNPs were characterized by a UV, IR, TEM, particle size analyzer and zeta potential measurement. *In vitro* stability of the PAuNPs was also analyzed. The hemo compatibility of PAuNPs was evaluated in human blood samples and the particles were found to be hemo compatible. The toxicity of the PAuNPs, 5-Fu and 5Fu@PAuNPs was analyzed in zebrafish embryos. The *in vitro* cytotoxicity of free 5-Fu, 5Fu@PAuNPs-Fa was investigated against MCF-7 cells (breast cancer) and it was observed that the amount of 5-Fu required to achieve 50% of growth of inhibition (Ic50) was much lower when compared to free 5-Fu [25].

Report on: A.Muthuvel, *Et al.* “Biosynthesis of gold nanoparticles using Solanum nigrum leaf extract and screening their free radical scavenging and antibacterial properties.”

The development of environmentally benign biological process for the synthesis of nanoparticles is one of the most important areas of research in nanotechnology. In the present study, gold nanoparticles (Au-NPs) were synthesized at room temperature using Solanum nigrum (*S. nigrum*) leaf extract as a reducing agent. The gold nanoparticles obtained were characterized by UV-visible spectroscopy, dynamic light scattering (DLS), zeta potential (ZP), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The Au-NPs formation was confirmed by UV-visible spectroscopy through color conversion due to surface plasma resonance band at 537 nm. DLS studies revealed that the average size of Au-NPs was found to be around 50 nm.

Zeta potential value for Au-NPs obtained was  $-17.80$  mV indicating the moderate stability of synthesized nanoparticles. The crystalline nature of the Au-NPs in face centered cubic structure is evident from the selected area electron diffraction (SAED) and XRD pattern. FT-IR spectrum identifies the presence of different biomolecules in the *S. nigrum* leaf extract responsible for the reduction and stabilization of Au-NPs. The biomedical properties of Au-NPs were premeditated as free radical scavenging activity and antibacterial static agents. Biosynthesized Au-NPs showed a strong DPPH radical and hydroxyl radical scavengers compared to the aqueous leaf extract of *S. nigrum*. Furthermore, the biosynthesized Au-NPs significantly inhibited the growth of medically important pathogenic Gram positive bacteria (*Staphylococcus saprophyticus* and *Bacillus subtilis*) and Gram negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*). The report suggests that the biosynthesized gold nanoparticles have enormous potential for use in the preparation of drugs used against various diseases and also a promising candidate for many medical applications [26].

Report on: M. R. Bindhu, *Et al.* “Antibacterial activities of Hibiscus cannabinus stem-assisted silver and gold nanoparticles.”

The synthesis of silver (Ag) and gold (Au) nanoparticles (NPs) using Hibiscus cannabinus stem extract was studied. The synthesized NPs were characterized using UV–visible spectroscopy (UV–vis), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). The surface plasmon resonance (SPR) peak of synthesized NPs was observed at 444 nm and 547 nm corresponding to AgNPs and AuNPs respectively. The prepared AgNPs and AuNPs were almost spherical in shape with an average particle size of 10 nm and 13 nm respectively. The FTIR study reveals that the carboxylic acid present in *H. cannabinus* stem extract has been used as reducing agent. The observed antibacterial properties suggest the possible utilization of prepared NPs in water purification [27].

Report on: A. Annamalai, *Et al.* “Green synthesis, characterization and antimicrobial activity of Au NPs using Euphorbia hirta L. leaf extract.”

The activity of a nano-sized particle is said to be greater when compared to that of its parent materials combined. Thus, an attempt was made to produce gold nanostructures having unusual physico chemical properties. In this study, eco-friendly, non-toxic gold nanoparticles (Au NPs) were biologically synthesized using the leaf extract of *Euphorbia hirta* L. The

synthesis of Au NPs was confirmed by a change in extract color from pale yellow to purple, and the surface plasmon resonance spectra obtained in a range of approximately 530 nm. Nanoparticles, whose sizes ranged from 6 nm to 71 nm, were synthesized. Different instrumental techniques were used to characterize the synthesized AuNPs, such as: TEM, XRD, EDAX, AFM, particle size analyzer, FTIR and Raman spectra. Also the antibacterial activity of the green synthesized Au NPs against bacterial strains of *Escherichia coli*, *Pseudomonas aeruginosa* and *Klebsiella pneumonia* was studied using the MIC method, and found to be highly effective [28].

Report on: Chidambaram Jayaseelan, *Et al.* “Green synthesis of gold nanoparticles using seed aqueous extract of *Abelmoschus esculentus* and its antifungal activity.”

The present work describes the synthesis of gold nanoparticles (Au NPs) using seed aqueous extract of *Abelmoschus esculentus* and its antifungal activity. UV–visible spectroscopy, XRD, FTIR, AFM, FESEM and EDX analyses were performed to ascertain the formation of Au NPs. The synthesized Au NPs were characterized by a peak at 536 nm in the UV–visible spectrum. XRD confirmed the crystalline nature of the nanoparticles of 62 nm size. The XRD peaks at 38°, 44°, 64° and 77° can be indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) Bragg’s reflections of cubic structure of metallic gold, respectively. The FTIR result clearly showed that the extracts containing OH as a functional group act in capping the nanoparticles synthesis. AFM shows the 3D topological characteristics of Au NPs. FESEM images revealed that all particles were spherical with a narrow size range of 45–75 nm. The antifungal activity of Au NPs was tested against *Puccinia graminis tritici*, *Aspergillus flavus*, *Aspergillus niger* and *Candida albicans* using the standard well diffusion method. The maximum zone of inhibition was observed in the Au NPs against *P. Graminis* (17 mm) and *C. albicans* (18mm). The results suggest that the synthesized Au NPs act as an effective antifungal agent. It is confirmed that Au NPs are capable of rendering high antifungal efficacy and hence have great potential in the preparation of drugs used against fungal diseases [29].

Report on: YonghongWang, *Et al.* “Barbated Skullcup herb extract-mediated biosynthesis of gold nanoparticles and its primary application in electrochemistry.”

The design, synthesis, characterization and application of biologically synthesized nanomaterials have become an important branch of

nanotechnology. This paper reports on the extracellular synthesis of gold nanoparticles using Barbated Skullcup (BS) herb (a dried whole plant of *Scutellaria barbata* D. Don) as the reducing agent. After exposing the gold ions to BS herb extract, rapid reduction of gold ions is observed leading to the formation of gold nanoparticles in solution. UV–vis spectrum of the aqueous medium containing gold nanoparticles showed a peak at around 540 nm. Transmission electron microscopy (TEM) micrograph analysis of the gold nanoparticles indicated that they were well-dispersed and ranged in size from 5–30 nm. When the gold nanoparticles were modified on the glassy carbon electrode (GCE), it could enhance the electronic transmission rate between the electrode and the p-nitrophenol [30].

## 2. Palladium

Report on: D.S. Shenya, *Et al.* “Rapid green synthesis of palladium nanoparticles using the dried leaf of *Anacardium occidentale*.”

A rapid, one pot and biogenic fabrication of Pd nanoparticles is here reported. Pd nanoparticles of below 5 nm in size are synthesized using the dried leaf powder of *Anacardium occidentale*. Rapid reduction results in the formation of spherical particles. The nanoparticles are characterized by XRD, TEM, UV–visible and FTIR analysis. The absorption spectra have continua that are characteristic of Pd nanoparticles. The broad nature of the XRD pattern arising due to reflections from the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes indicate the crystallinity of the nanoparticles with face centered cubic (fcc) structure. The morphology and shape of the nanoparticles are obtained by analyzing TEM images. Most of the nanoparticles are spherical, with a size in the range 2.5 and 4.5 nm. FTIR spectra of dried Pd nanoparticles, native and treated dried leaf powder have been analyzed to determine the biomolecule responsible for the reduction of Pd<sup>2+</sup> and capping of the palladium nanoparticles. The possible mechanism of formation of the nanoparticles is suggested [31].

Report on: Mujeeb Khan, *Et al.* “Biogenic synthesis of palladium nanoparticles using *Pulicaria glutinosa* extract and their catalytic activity towards the Suzuki coupling reaction.”

Green synthesis of nanomaterials has the edge over chemical methods due to its environmental compatibility. Herein, we report on an eco-friendly method for the synthesis of palladium (Pd) nanoparticles (NPs) using an aqueous solution of *Pulicaria glutinosa*, a plant widely found in a large region of Saudi Arabia, as a bioreductant. The as prepared Pd NPs were

characterized using ultraviolet-visible (UV-vis) spectroscopy, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FT-IR). The hydroxyl groups of the plant extract (PE) molecules were found to be mainly responsible for the reduction and growth of Pd NPs. FT-IR analysis confirmed the dual role of the PE, both as a bioreductant as well as a capping ligand, which stabilizes the surface of Pd NPs. The crystalline nature of the Pd NPs was identified using XRD analysis, which confirmed the formation of a face centered cubic structure (JCPDS: 87-0641, space group: Fm3m (225)). Furthermore, the as-synthesized Pd NPs demonstrated excellent catalytic activity towards the Suzuki coupling reaction under aqueous and aerobic conditions. Kinetic studies of the catalytic reaction monitored using GC confirmed that the reaction is completed in less than 5 mins [31].

Report on: Ramesh Kumar Petla, *Et al.* “Soybean (*Glycine max*) Leaf Extract Based Green Synthesis of Palladium Nanoparticles.”

Palladium (Pd) nanoparticles were synthesized using protein-rich soybean leaf extract based biological process. Reduction of palladium ions by soybean leaf extract was examined by the UV-visible spectroscopic technique. It was believed that the proteins and some of the amino acids that exist in soybean leaf extracts were actively involved in the reduction of palladium ions. Furthermore, it was confirmed by Fourier transform infrared spectroscopic (FTIR) analysis. These amino acids are not only involved in the reduction of palladium ions but also act as surfactants that inhibit the rapid agglomeration. The phase purity of the synthesized palladium nanoparticles was investigated through X-ray Diffraction (XRD) analysis and the obtained pattern was compared with JCPDS data. Transmission electron microscopic (TEM) images of the palladium particles were recorded and the particle size was found to be ~15 nm [33].

Report on: Malathi. Ra and Ganesan.V. “Biological synthesis of palladium nanoparticles using leaf extract of *Sebastiania chamaelea* (L.) Muell. Arg.”

This report studies the biological synthesis of palladium nanoparticles with the help of the *Sebastiania chamaelea* (L.) Muell. Arg. (Family: Euphorbiaceae) leaf. Aqueous leaf extract of *Sebastiania chamaelea* was employed for the bioreduction of Pd<sup>2+</sup> ions to Pd<sup>0</sup>. The leaf was collected from the campus of Ayya Nadar Janaki Ammal College, Sivakasi, Tamil Nadu. 10ml of leaf extract was prepared, resuspended in 90ml of palladium chloride solution as it is known as reaction medium. The color

change of the reaction medium from pale yellow to dark brown during the incubation period is due to the vibrations in surface plasmon resonance (SPR). It indicates the formation of palladium nanoparticles. From this reaction medium, a small aliquot of the sample was used for the characterization of palladium nanoparticles through UV-Visible (UV-Vis) Spectroscopic analysis, Fourier transform infrared (FTIR) spectral analysis, X-ray diffraction (XRD) analysis and a scanning electron

microscope (SEM) with energy dispersive X-ray (EDX) analysis. The SPR with  $\lambda$  max at 475 nm and the absorbance was raised up to 0.78a.u. The FTIR analysis explains that the biomolecules responsible for the stability of palladium nanoparticles that are synthesized by the leaf broth. The XRD analysis gives the structural information of nanoparticles. The SEM and EDAX analyses confirmed the significant presence of palladium nanoparticles. The size of the particle ranged from 50 to 80 nm. Thus the synthesis of palladium nanoparticles of various sizes is achieved using the leaf broth of *Sebastiania chamaelea*, as a green route due to its eco-friendly nature, and the method does not involve any toxic methods or chemicals in the synthesis of palladium nanoparticles [34].

Report on: K. Anand, *Et al.* "Biosynthesis of palladium nanoparticles by using *Moringa oleifera* flower extract and their catalytic and biological properties."

The biosynthesis of nanostructured bio palladium nanoparticles (PdNPs) from an aqueous solution of crystalline palladium acetate is here reported. For the synthesized PdNPs in solution, an agro forest biomass waste petal of *Moringa oleifera* derived bis-phthalate was used as natural reducing and biocapping agent. Continuous absorption in the UV region and subsequent brown color change confirmed the formation of PdNPs. A strong surface plasmon peak for PdNPs occurred at 460 nm. PdNPs were characterized by SEM with EDX, FTIR, TEM and DLS. The chemical composition of the aqueous extract was determined by GC-MS coupled with FTIR and INMR. The catalytic degradation effect by Pd NPs on the industrial organic toxic effluents p-nitrophenol (PNP) and methylene blue dye was monitored by UV Spectroscopy. On the other hand, PdNPs catalysed the base mediated Suzuki coupling reaction for biphenyl synthesis in water. Moreover, PdNPs were found to be reusable catalysts. Toxicity studies of PdNPs showed that the death of brine shrimp to be less than 50%. Therefore, PdNPs displayed the potential for further anti-cancer studies via tumor cell lines. The *in vitro* cytotoxicity evaluation of the extract-capped nanoparticles was carried out using human lung carcinoma cells (A549)

and peripheral lymphocytes normal cells by MTT cell viability assay. Also, PdNPs showed antibacterial activity against *Enterococcus faecalis* among the different tested strains, including *Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans* and *Candida utilis* [35].

Report on: Farzaneh Arsiya, *Et al.* “Green synthesis of palladium nanoparticles using *Chlorella vulgaris*.”

In this paper the green synthesis of palladium nanoparticles by *Chlorella vulgaris* aqueous extract was studied. The synthesis of palladium nanoparticles was observed over a 10-minute period. The properties of synthesized nanoparticles were confirmed by transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and UV-spectroscopy. The formation of palladium nanoparticles was confirmed by the presence of an absorption peak between 410-420 nm using a UV-visible spectrophotometer. The TEM image revealed that the average particle size is 15 nm, whereas others were in the range of 5 to 20 nm. The nanoparticles were crystalline in nature, which was confirmed by XRD pattern. FT-IR indicated that polyol and amide groups present in *C. vulgaris* may have participated in the synthesis of palladium nanoparticles. So, functional groups have a critical role in reducing the metal ions in an eco-friendly and non-toxic process [36].

Report on: Ashok Bankar, *Et al.* “Banana peel extract mediated novel route for the synthesis of palladium nanoparticles.”

Bio-inspired palladium nanoparticles were synthesized by using banana peel extract (BPE), a non-toxic eco-friendly material. Boiled, crushed, acetone precipitated, air-dried peel powder was used to reduce palladium chloride. The palladium nanoparticles were characterized by using UV-Visible spectroscopy, scanning electron microscope-energy dispersive spectra (SEM-EDS) and X-ray diffraction (XRD) analysis. Dynamic light scattering (DLS) studies revealed the average size of nanoparticles to be 50 nm. Fourier transform infrared spectroscopy (FTIR) implied the role of carboxyl, amine and hydroxyl groups in the synthetic process. This paper thus describes a novel green method for the synthesis of palladium nanoparticles [37].

Report on: E. Ismail, *Et al.* “Green palladium and palladium oxide nanoparticles synthesized via *Aspalathus linearis* natural extract.”

This contribution represents the first synthesis of nano-scaled Pd and PdO by a completely green process using *Aspalathus linearis* natural plant extract as an effective bioreducing as well as a capping agent. Their sphere-like size was found to range within ( $\text{\O}$ particles) =3.8-22 nm. Their morphological, structural and optical properties were investigated using various complementary surface/interface characterization techniques such as HR-TEM, DSC, XRD, EDS, XPS, and Raman spectroscopy. The results confirmed the formation of single fcc Pd and pure tetragonal PdO nanocrystals upon annealing at 100 and 600°C in standard air conditions. It was found that the dynamic of the complete oxidation of the bio-synthesized Pd nanocrystals into single phase PdO is very fast, ~2hrs instead of 10-20 hrs, typically [38].

Report on: Aasaithambi Kalaiselvi, *Et al.* “Synthesis and characterization of palladium nanoparticles using *Catharanthus roseus* leaf extract and its application in the photo-catalytic degradation.”

The potential effect of *Catharanthus roseus* leaf extract for the formation of palladium nanoparticles and its application on dye degradation was discussed. The efficiency of *C. roseus* leaves was used as a bio-material for the first time as reducing agent. Synthesized palladium nanoparticles were supported by UV–vis spectrometry, XRD, FT-IR and TEM analysis. The secondary metabolites responsible for the formation of nanoparticles were identified by GC–MS. The results showed that the effect of time was directly related to synthesized nanoparticles, and that functional groups have a critical role in reducing the metal ions and in stabilizing the palladium nanoparticles in an eco-friendly process [39].

Report on: Sadaf Lebaschi, *Et al.* “Green synthesis of palladium nanoparticles mediated by black tea leaves (*Camellia sinensis*) extract: Catalytic activity in the reduction of 4-nitrophenol and Suzuki-Miyaura coupling reaction under ligand-free conditions.”

The present study was conducted to synthesize palladium nanoparticles (Pd NPs) through a green route using non-toxic and renewable natural black tea leaf (*Camellia sinensis*) extract as the reducing and stabilizing agent. The as-prepared Pd@B.tea NPs catalyst was characterized by UV–vis spectroscopy, X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), field emission scanning electron microscopy



(FESEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The Pd@B.tea NPs catalyst could be used as an efficient and heterogeneous catalyst for Suzuki coupling reactions between phenylboronic acid and a range of aryl halides (X = I, Br, Cl) and also the reduction of 4-nitrophenol (4-NP) using sodium borohydride in an environment-friendly medium. Excellent yields were obtained with a wide range of substrates, and the catalyst was recycled 7 times without any significant loss of its catalytic activity [40].

Report on: K. Mallikarjuna, *Et al.* “Palladium nanoparticles: Single-step plant-mediated green chemical procedure using Piper beetle leaves broth and their anti-fungal studies.”

The green synthesis of metal nanoparticles has made considerable progress in recent years due to its novel optical, catalytic, hydrogen storage, bio-imaging and electrochemical applications. In recent years the utilization of phyto-organic moieties from different biological sources has utilized modern technology for the nanoparticles synthesis. The authors synthesized the palladium nanoparticles (PdNPs) using Piper beetle leaf extract as a reducing and capping material, this can reduce the toxic chemicals, the multiple steps in the synthesis procedure, and is environmentally harmless. The surface plasmon resonance of growing PdNPs was investigated by UV-Vis spectroscopy. The particle morphology, distribution and size were estimated by transmission electron microscopy and the particle size is found to be  $4 \pm 1$  nm, the phase purity of synthesized PdNPs was characterized by selected area electron diffraction and X-ray diffraction patterns. The presences of the bio-organic moieties, which are responsible for wrapping around the PdNPs and probable pathway of the synthesis analyzed with the Fourier transform infrared (FTIR) spectroscopy. The study concluded that water-soluble flavonoids of P. beetle are responsible for phyto-reduction of PdNPs. The bioactivity demonstrated by synthesized PdNPs suggests excellent clinical usage as anti-fungal material [41].

Report on: Mahmoud Nasrollahzadeha, *Et al.* “Green synthesis of palladium nanoparticles using Hippophae rhamnoides Linn leaf extract and their catalytic activity for the Suzuki–Miyaura coupling in water.”

This study reports on the green synthesis of palladium nanoparticles using Hippophae rhamnoides Linn leaf extract and their application as heterogeneous catalysts for the Suzuki–Miyaura coupling in water. The synthesized nanoparticles are characterized by XRD, SEM, TEM and UV–

vis techniques. This method has the advantages of high yields, simple methodology, and the elimination of ligand, organic solvent and homogeneous catalysts, and easy work-up. Furthermore, the catalyst exhibits high catalytic activity, superior cycling stability and excellent substrate applicability [42].

Report on: G. Sharmila, *Et al.* “Green synthesis, characterization and antibacterial efficacy of palladium nanoparticlessynthesized using *Filicium decipiens* leaf extract.”

The synthesis of metal nanoparticles through green chemistry route is an emerging eco-friendly approach in contemporary research. An eco-friendly, biogenic synthesis of palladium nanoparticles (PdNPs) using *Filicium decipiens* leaf extract was reported in the present study. The synthesized PdNPs were characterized by UV-visible spectroscopy, transmission electronmicroscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The PdNPs formation was confirmed by a UV-visible spectrophotometer and spherical shaped PdNPs with a size range of 2-22 nm were observed in TEM analysis. Energy dispersive X-ray spectroscopy (EDS) analysis confirmed the presence of palladium in the synthesized nanoparticles. The crystalline nature of PdNPs was confirmed by XRD pattern and compared with the standard. The phytochemicals and proteins were identified by their functional groups in FT-IR spectrum and revealed the amide, amine groups present in *F. decipiens* may have interfered with in the bio-reduction reaction for PdNPs synthesis. Prepared PdNPs showed potential antibacterial activity against both Gram positive and Gram negative bacteria. *F. decipiens* leaf extract based PdNPs showed high bactericidal activity against *Escherichia coli* and *Pseudomonas aeruginosa*, as compared to *Staphylococcus aureus* and *Bacillus subtilis* where results showed that phytochemicals rich *F. decipiens* leaf extract may be utilized as an effective non-toxic reducing agent for PdNPs synthesis and prepared PdNPs may be useful in biomedical applications [43].

Report on: T.V. Surendra, *Et al.* “RSM optimized *Moringa oleifera* peel extract for green synthesis of *M. oleifera* capped palladium nanoparticles with antibacterial and hemolytic property.”

Palladium nanoparticles (Pd NPs) are very good catalytic agents in many coupling reactions; also they are very effective biological agents against bacteria and fungus. *M. oleifera* capped Pd NPs were synthesized from the microwave assisted methanolic extract of *M. oleifera* peel. To optimize the

extraction process RSM (response surface methodology) was applied. To get a good extraction yield BBD (Box-Behnken design) was employed. The better optimized conditions for the extraction was found as 400 W, 25ml of CH<sub>3</sub>OH at 65°C for 2 mins. The researchers recorded a 61.66mg of extract yield from this method. Eco-friendly *M. oleifera* capped Pd NPs were synthesized using *M. oleifera* peel extract and confirmed using the different characterization techniques such as UV- Vis spectroscopy, XRD, SEM and HR-TEM analysis. They found the size of the *M. oleifera* capped Pd NPs nanoparticles to be 27 ±2 nm and the shape of the particles as spherical through the TEM analysis. *M. oleifera* capped Pd NPs exhibit good antibacterial activity against *S. aureus* (*Staphylococcus aureus*) and *E. coli* (*Escherichia coli*) bacterial strains, and the zone inhibition was found to be 0.6 and 0.7mm. The synthesized *M. oleifera* capped Pd NPs are screened for haemolytic activity, proving that the *M. oleifera* capped Pd NPs are non-toxic on RBCs cells [44].

Report on: Kamran Tahir, *Et al.* “*Sapium sebiferum* leaf extract mediated synthesis of palladium nanoparticles and in vitro investigation of their bacterial and photocatalytic activities.”

There is a growing need to introduce eco-friendly and sustainable procedures for the synthesis of metal nanoparticles that include mild reaction conditions, simple reaction set-up, use of non-toxic media such as water and plant extract, cost effectiveness, as well as greater efficiency for biomedical and catalytic applications. For this purpose, small and highly dispersed palladium nanoparticles (PdNPs) were prepared by an eco-friendly and cost effective green method using water-soluble leaf extract of *Sapium sebiferum* as a reducing and capping agent. The formation of PdNPs was optimized at various temperatures i.e. (30°C, 60°C and 90°C) and different concentrations of leaf extract (5ml and 10ml) in order to control their size and shape. The results indicated that the PdNPs synthesized at 10ml leaf extract concentration and 60°C temperature have a small size (5 nm) and spherical shape. The nanoparticles formation, their dispersion, size and shape were confirmed by various characterization techniques i.e. UV-Vis spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), thermo gravimetric analysis (TGA) and dynamic light scattering technique (DLS) analysis. The biologically synthesized PdNPs were tested for size-dependent photo degradation of methylene blue and inactivation of bacteria. The PdNPs synthesized at optimized condition (10ml extract concentration and 60°C) have strong photo catalytic activity and reduced

90% methylene blue in 70 mins. The optimized PdNPs also showed strong bacterial inhibition against *Staphylococcus aureus* 29( $\pm 0.8$  mm), *Bacillus subtilis* 19 ( $\pm 0.6$  mm) and *Pseudomonas aeruginosa* 11( $\pm 0.6$  mm). The results of this examination demonstrate effective applications of extremely active PdNPs [45].

### 3. Platinum

Report on: Jae Yong Song, *Et al.* “Biological synthesis of platinum nanoparticles using *Diopyros kaki* leaf extract.”

The leaf extract of *Diopyros kaki* was used as a reducing agent in the eco-friendly extracellular synthesis of platinum nanoparticles from an aqueous  $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$  solution. A greater than 90% conversion of platinum ions to nanoparticles was achieved with a reaction temperature of  $95^\circ\text{C}$  and a leaf broth concentration of 10%. A variety of methods were used to characterize the platinum nanoparticles synthesized: inductively coupled plasma spectrometry, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy (FTIR). The average particle size ranged from 2 to 12 nm depending on the reaction temperature and concentrations of the leaf broth and  $\text{PtCl}_6^{2-}$ . FTIR analysis suggests that platinum nanoparticle synthesis using *Diopyros kaki* is not an enzyme-mediated process. This is the first report of platinum nanoparticle synthesis using a plant extract [46].

Report on: T. Riddin, *Et al.* “Biological synthesis of platinum nanoparticles: Effect of initial metal concentration.”

The unusual and novel properties of metal nanoparticles are highly sought-after in a number of new and existing industries. Current chemical methods of nanoparticle synthesis have shown limited success and it is hoped that the use of a biological approach may overcome many of these obstacles. The exploitation of micro-organisms for the biosynthesis of metal nanoparticles is an area of research that has received increasing attention over the last decade. The use of living microbes as a tool for nanoparticle biosynthesis has been researched extensively; however, the use of the cellular extract within the cells, excluding the living organism as a whole, has not received comparable attention. In this investigation, the cellfree, cell-soluble protein extract from a consortium of sulphate-reducing bacteria was used successfully in the biosynthesis of geometric Pt(0) nanoparticles, where previously, whole cells from the same culture

had only resulted in amorphous Pt(0) deposits. It appears that by removing the spatial restrictions imposed by the cell itself, nanoparticles could form. It was also found that by altering the ratio of Pt(IV) to protein concentration in solution, a variety of particle morphologies resulted [47].

Report on: Rajesh W Raut, *Et al.* "Rapid biosynthesis of platinum and palladium metal nanoparticles using root extract of *Asparagus racemosus* Linn."

The fabrication of metal nanoparticles is undergoing a revolutionary change due to its widespread application in such areas as: selective and specific catalysis, hydrogenation, optoelectronics, semiconductors, sensing and diagnosis. Biologically, the metal nanoparticles are produced using fungi, yeasts, bacteria, algae and plant biomass. The metal nanoparticles synthesized using biological methods include mainly silver and gold. The synthesis of metals such as platinum and palladium is still unexplored. It is within this context that the present study has synthesized platinum and palladium metal nanoparticles using the root extract of *Asparagus racemosus* Linn. at room temperature. The synthesized metals were characterized using UV-visible spectroscopy, transmission electron microscopy (TEM) and cyclic voltammetry (CV) techniques. UV-Visible study revealed that in both cases nanoparticles are produced within 5 mins. TEM study shows that metal the nanoparticles formed are crystalline in nature and spherical in shape. It also shows that Pt and Pd nanoparticles are nearly monodispersed, having a particle size ranging between 1 to 6 nm. The CV of the metal nanoparticles shows reversible redox behavior. The method reported for the synthesis of metal nanoparticles is clean, rapid and eco-friendly [48].

Report on: Bingyun Zheng *Et al.* "Plant-mediated synthesis of platinum nanoparticles and its bioreductive mechanism."

In this research Pt nanoparticles (PtNPs) were biologically synthesized by reducing Na<sub>2</sub>PtCl<sub>4</sub> with *Cacumen Platycladi* Extract (CPE). The effects of reaction temperature, initial Pt(II) concentration, CPE percentage on Pt(II) conversion and the size distribution of the PtNPs were studied. The results showed that the Pt(II) conversion rate reached 95.9% and that PtNPs measuring  $2.4 \pm 0.8$  nm were obtained under the following conditions: reaction temperature, 90°C; CPE percentage, 70%; initial Pt(II) concentration, 0.5 mM; reaction time, 25 hrs. In addition, the bioreduction of Pt(II) was attributed to reducing sugars and flavonoids rather than proteins. The elucidation of bioreductive mechanism of Pt(II) ions was

achieved by investigating the changes that occurred in the reducing sugar, flavonoid and protein concentrations in the plant extract, leading to good insights into the formation mechanism of such biosynthesized PtNPs [49].

Report on: John Leo Anyik, *et al.* “Plant-mediated synthesis of platinum nanoparticles using water hyacinth as an efficient biomatrix source: An eco-friendly development.”

Herein is reported an eco-friendly synthesis of platinum nanoparticles (Pt-NPs) using aqueous extracts from water hyacinth plants used as efficient reducing and stabilizing agents. The color change and optical analysis confirmed the formation of Pt-NPs. Transmission electron microscope (TEM) analysis showed that the as-synthesized Pt-NPs are small and spherical in shape with an average diameter of 3.74 nm; while dynamic light scattering (DLS) analysis showed hydrodynamic size and zeta potential of 73.3 nm and  $-0.0536$  mV respectively. Fourier transform infrared spectroscopy (FTIR) indicated that the presence of hydroxyl, nitrogen and carbohydrate groups present in the extract are responsible for the reduction and capping of Pt-NPs [50].

Report on: Renata Dobručka, “Biofabrication of platinum nanoparticles using *Fumariae herba* extract and their catalytic properties”

Due to the increasing popularity of using plant extract in the synthesis of nanoparticles this study presents the synthesis of platinum nanoparticles using *Fumariae herba* extract. The formation of platinum nanoparticles was confirmed by UV–visible spectroscopy (UV–Vis), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) with EDS profile. Transmission electron micrograph presented the hexagonal and pentagonal shape of the synthesized nanoparticles sized about 30 nm. Moreover, platinum nanoparticles presented good catalytic properties in the reduction of methylene blue and crystal violet [51].

Report on: Hayrunnisa Nadaroglu, *Et al.* “Green synthesis and characterisation of platinum nanoparticles using quail egg yolk.”

Nanotechnology is extensively used in all domains today. Therefore, nano synthesis is also significant in all fields currently under exploration. The results of studies already conducted have revealed that nanoparticle synthesis is performed by using both chemical and physical methods. It is well known that these syntheses are carried out at high charge pressure and temperature in harsh environments. Therefore, this study investigated a

green synthesis method that can be sustained in milder conditions. In this research, quail egg yolk, having high vitamin and protein content, was prepared for green synthesis reaction and used for the synthesis of platinum nanoparticles in the reaction medium. Reaction situations were optimized as a function of pH, temperature, time and concentration by using quail egg yolk. The results showed that the highest platinum nanoparticles were synthesized at 20°C and pH 6.0 for 4 hrs. Also, optimal concentration of metal ions was established as 0.5 mM. The synthesized platinum nanoparticles were characterised by using UV spectrum, X-ray diffraction and scanning electron microscope [52].

Report on: A. Thirumurugan, *Et al.* “Green synthesis of platinum nanoparticles using *Azadirachta indica*: An eco-friendly approach.”

Developing an economic and eco-friendly procedure for metallic nanoparticles synthesis is an important branch of nanobiotechnology. In the present study, the biological synthesis of noble platinum nanoparticles and their characterization using neem extracts was investigated. The formations of nanoparticle dispersions were characterized by a UV–visible spectrophotometer. TEM analysis showed the formation of nanoparticles in the range of 5–50 nm with polydispersed small to large spheres. FT-IR measurement revealed that the proteins are the possible biomolecules responsible for the reduction of chloroplatinic ion into platinum nanoparticles. The present study proved that medicinally valuable neem extracts have the capability to synthesize platinum nanoparticles and, moreover, this green route makes it an easier and more cost effective method [53].

Report on: Palanivel Velmurugan, *Et al.* “*Prunus x yedoensis* tree gum mediated synthesis of platinum nanoparticles with antifungal activity against phytopathogens.”

Green synthesis of platinum nanoparticles (PtNPs) using *Prunus x yedoensis* tree gum extract was studied. Color changes, ultraviolet–visible spectra (277 nm), X-ray diffraction peaks ( $2\theta=38.17, 45.54,$  and  $68.12$ ), and Fourier transform infrared spectroscopy confirmed the presence of PtNPs. Transmission electron microscopy shows that PtNPs are mostly spherical and oval in shape, with an average particle size of 10 to 50 nm. Chemical constituents present in the gum extract may be responsible for the reduction of Pt ion. Among the five phytopathogens tested the two pathogens *Colletotrichum acutatum* and *Cladosporium fulvum* show

15mm and 18mm zones of inhibition against synthesized PtNPs at 4 and 8 $\mu$ g/well, respectively [54].

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# CHAPTER THREE

## MATERIALS AND METHODS FOR AU, PD, PT NANOPARTICLES

### 1. Gold

*Acalypha indica* Linn: Biogenic synthesis of silver and gold nanoparticles and their cytotoxic effects against MDA-MB-231, human breast cancer cells.

#### a) Preparation of extract

10g of freshly collected *A. indica* leaves were surface cleaned with running tap water followed by distilled water and boiled in 100ml of distilled water at 60°C for 5 mins. Then, the extract was filtered and used for the biogenic synthesis of both silver and gold nanoparticles.

#### b) Biogenic synthesis and characterization of silver nanoparticles

The biogenic synthesis of silver and gold nanoparticles was performed according to the standard published procedure with slight modifications. The methods for the biosynthesis and characterization of silver nanoparticles from the leaf extract of *A. indica* were given in our previously published paper.

#### c) Biogenic synthesis and characterization of gold nanoparticles

For gold nanoparticles biosynthesis, 1 mM HAuCl<sub>4</sub> was added to the broth containing 36ml of leaf extract and 64ml of distilled water at neutral pH. After this, the solution was kept at 37°C under static conditions. Simultaneously, a control setup was maintained without adding HAuCl<sub>4</sub>. The pinkish violet color that formed after the addition of HAuCl<sub>4</sub> was characterized using a UV-vis spectrophotometer (Beckman DU-20 spectrophotometer) in the range of 200–700 nm. Further, the reaction mixture was subjected to centrifugation at 75,000 × g for 30 mins and the resulting pellet was dissolved in de-ionized water and filtered through a

millipore filter (0.45mm). An aliquot of this filtrate containing gold nanoparticles was used for FE–SEM (field emission–scanning electron microscopy), TEM (transmission electron microscopy) and XRD (X-ray diffraction) analyses. For electron microscopic studies, 25ml of the sample was sputter coated on copper stub and the size as well as shape of the gold nanoparticles were studied using FE-SEM and TEM. For XRD studies, dried gold nanoparticles were coated on an XRD grid, and the spectra were recorded using Philips PW 1830 X-ray generators operated at a voltage of 40kV and a current of 30mA with Cu K $\alpha$  radiation. [1].

Blue green alga mediated synthesis of gold nanoparticles and its antibacterial efficacy against Gram positive organisms.

a) Preparation of extract

For the protein extraction, 1g of dry *S. platensis* powder was mixed with 10ml of millipore water and ground using mortar and pestle. The mixture was centrifuged at 5000 rpm for 10 mins. The supernatant was used for synthesis of AuNPs and the amount of protein present was quantitatively estimated by Lowry's method.

b) Synthesis of AuNPs

For the synthesis of AuNPs, *S. platensis* protein extract was added to 10mM HAuCl $_4$ •3H $_2$ O solution in a ratio of 1:1 (10ml: 10ml) followed by the addition of 1 N NaOH under stirring condition. On addition of 1 N NaOH, there was an immediate color change from green to greenish yellow and was maintained under constant stirring for 3 hrs. and incubated at room temperature for 48 hrs. The appearance of a ruby red color indicated the formation of AuNPs [2].

Green synthesis of gold nanoparticles using *Cucumis sativus* (Cucumber) aqueous extract.

a) Preparation of Cucumber aqueous extract

In our synthesis procedure, cucumber aqueous extract was used as a reducing and capping agent. The extract was prepared by soaking 2g of cucumber in 20ml of de-ionized water overnight, and then crushing it with a mortar and pestle, the mixture was boiled for 10-15 mins at 70-80°C. The extract was followed by centrifuge for 15 mins at 5000 rpm; collected supernatant was then filtered by a standard sterilized filtration method. The extract was then stored at 4°C for further use.

### b) Synthesis of gold nanoparticles

In a typical experiment, AuNPs synthesis protocol was optimized by stirring a mixture of cucumber aqueous extract at three different concentrations with 1mM HAuCl<sub>4</sub> aqueous solution (1:1, 5:1, 10:1) at 200 rpm at room temperature for 1 hr. Within this time period a change in color was observed, indicating nanoparticle synthesis [3].

Green synthesis of gold nanoparticles using *elettaria cardamomum* (ELAICHI) aqueous extract.

#### a) Preparation of Elaichi aqueous extract

Extract prepared by soaking 2gm of seed pod in 20ml of de-ionized water overnight, crushing it with mortar and pestle. The mixture was then boiled for 10-15 mins at 70-80°C. The extract was followed by centrifuge for 15 mins at 5000 rpm, collected supernatant was then filtered by the standard sterilized filtration method. The extract was then stored at 4°C for further use.

### b) Synthesis of Gold Nanoparticles

In a typical experiment, AuNPs synthesis protocol was optimized by stirring a mixture of elaichi aqueous extract at three different concentrations with 1mM HAuCl<sub>4</sub> aqueous solution (1:1, 5:1, 10:1) at 200 rpm at room temperature for 1 hr. During this time period a change in color was observed, indicating nanoparticle synthesis [4].

Green Synthesis of Gold Nanoparticles using Neem (*Azadirachta indica* L.) Leaf Extract and its Biomedical Applications.

#### a) Ethanolic Extract Preparation

Neem leaves or sticks (Figure 1A); 300gm were selected, washed, cut into small pieces and dried in an oven (45-50°C) for 3 days. Neem leaves or sticks were blended in a blender and then extracted using 96% ethanol 10h. The extraction was carried out using the soxhlet apparatus (60-80°C; 1:50, w/v) up until the last extract was colorless. The combined extract was filtered, and the filtrate was concentrated and evaporated under the same condition, as described before, to afford the soxhlet extract [55].



### b) Biological Synthesis of Gold Nanoparticles

The broth was used to effect a reduction of  $\text{Au}^{3+}$  ions to  $\text{Au}^0$  by using finely cut neem leaves (10g) in a 500ml Erlenmeyer flask with 40ml of sterile distilled water and it was boiled up to a 15 min maximum. In this research, 0.2ml of broth was added to 50ml of  $10^{-3}$  M aqueous chloroauric acid ( $\text{HAuCl}_4$ ) solution. The color of the solution changed to cherry red color within an hour (50 mins) [56] [5].

### Review: Green Synthesis of Silver and Gold Nanoparticles

#### a) Preparation and synthesis of AuNPs

An aqueous chloroauric solution ( $10^{-3}$  M) was added separately to the reaction vessels containing the ethanol extract of black tea and its tannin-free fraction (10% v/v) and the resulting mixture was allowed to stand for 15 mins. At room temperature Chloroauric acid was purchased from Merk, Darmstadt, Germany. The ethanol solution (10% v/v) was used as a negative control. The reduction of the  $\text{Au}^{+3}$  ions by these ethanol extract in the solutions was monitored by sampling the aqueous component (2ml) and measuring the UV-visible spectrum of the solutions. All samples were diluted three times with distilled water and the UV-visible spectra of these samples were measured on a Labomed Model UVD-2900 UVVIS Double Beam PC Scanning spectrophotometer, operated at are solution of 2nm.

In the synthesis of AuNPs, 10ml of the aqueous extract of *Gracilaria corticata* was added to 90ml of  $10^{-3}$  M aqueous  $\text{HAuCl}_4$  solution in 500ml Erlenmeyer flask and stirred for 4 hrs at 120 rpm at  $40^\circ\text{C}$ .

#### b) Preparation and Synthesis of AgNPs

In a typical reaction procedure, 5ml of plant extract was added to 100ml of  $1 \times 10^{-3}$  M aqueous  $\text{AgNO}_3$  solution, with stirring magnetically at room temperature. The yellow color of the mixture of silver nitrate and plant extract at 0 min of reaction time changed rapidly (at room temperature after 2 mins) to a black suspended mixture. The concentration of  $\text{AgNO}_3$  solution and leaf extract was also varied at 1 to 4 mM and 5% to 10% by volume, respectively. UVvisible (UV-vis) spectra exhibited a strong surface plasmon resonance (SPR) band at 420, thus indicating the formation of AgNPs. The AgNPs obtained by plant extract were centrifuged at 15,000 rpm for 5 mins, and were subsequently dissolved in sterile distilled water to remove any uncoordinated biological materials [57].[6].

## Review: Green Synthesis of Silver and Gold nanoparticles

### a) Synthesis of AuNPs

(a) An aqueous chloroauric acid solution ( $10^{-3}$ M) was added separately to the reaction vessels containing the ethanol extract of black tea and its tannin-free fraction (10% v/v), and the resulting mixture was allowed to stand for 15 mins at room temperature. Chloroauric acid was purchased from Merck, Darmstadt, Germany. The ethanol solution (10% v/v) was used as a negative control. The reduction of the  $\text{Au}^{+3}$  ions by these ethanol extracts in the solutions was monitored by sampling the aqueous component (2ml) and measuring the UV-visible spectrum of the solutions. All samples were diluted three times with distilled water and the UV-visible spectra of these samples were measured on a Labomed Model UVD-2950 UV-VIS Double Beam PC Scanning spectrophotometer, operated at a resolution of 2 nm. Furthermore, AuNPs were characterized by transmission electron microscopy (model EM 208 Philips) [58].

In the synthesis of AuNPs, 10ml of the aqueous extract of *Gracilaria corticata* was added to 90ml of  $10^{-3}$  M aqueous  $\text{HAuCl}_4$  solution in a 500ml Erlenmeyer flask, and then stirred for 4 hrs at 120 rpm at  $40^\circ\text{C}$ . Suitable controls were maintained throughout the conduct of experiments [59].

### b) Synthesis of AgNPs

In a typical reaction procedure, 5ml of plant extract was added to 100ml of  $1 \times 10^{-3}$  M aqueous  $\text{AgNO}_3$  solution, with stirring magnetically at room temperature. The yellow color of the mixture of silver nitrate and plant extract at 0 min of reaction time changed very rapidly at room temperature after 2 mins to a black suspended mixture. The concentrations of  $\text{AgNO}_3$  solution and leaf extract were also varied at 1 to 4 mM and 5% to 10% by volume, respectively. UV-visible (UV-vis) spectra showed a strong Surface plasmon resonance (SPR) band at 420 nm thus indicating the formation of AgNPs. The AgNPs obtained by plant extract were centrifuged at 15,000 rpm for 5mins and subsequently dispersed in sterile distilled water to get rid of any uncoordinated biological materials [60]. Polyphenols found in various plant extracts were used as reductants and as capping agents during synthesis. NPs in a single-step green synthesis process and biogenic reduction of metal ion to base metal is quite rapid, readily conducted at room temperature and pressure, and easily scaled-up [61,62] [7].

Studies of the catalytic, antioxidant, antibacterial and anticancer activities of biogenic gold nanoparticles

a) Preparation of extract

Dried Ac nuts are collected from a local market, followed by thorough washing with de-mineralised water. 15mg of the washed, finely powdered nuts of Ac are further boiled in 100ml de-mineralised water for 5 mins and filtered to get the aqueous nut extract. Chloroauric acid ( $\text{HAuCl}_4$ ) purchased from Sigma-Aldrich is used as the source of  $\text{Au}^{3+}$ .

b) Synthesis of gold nanoparticles

Gold colloids are synthesized at the constant concentration of the precursor solution and that of the reducing agent. The pH of the solution is set at 6. Temperature variation adopted for the synthesis includes 300 K and 373 K. To 30ml of  $2.5 \times 10^{-4}$  M chloroauric acid, 10ml of the aqueous nut extract is added at 300 K, with continued stirring for 5 mins. The appearance of a stable violet color after 4–5 h indicates the formation of GNPS (colloid A). The experiment is repeated at 373 K to obtain a red colored colloid B. Further, a mixture of the nut extract and precursor solution is irradiated with microwave radiation of frequency 2450 MHz, for 1 min to produce colloid C. The rapid formation of stable red colored gold colloid within 1 min of the addition of the nucleating agent is attained in both the cases (colloid B and C).

The synthesized colloids are found to be stable for two months [8].

Green phyto-synthesis of gold nanoparticles using *Achyranthes aspera* Linn seed-epicotyls layer extracts and its anti-cancer activity.

a) Preparation of *A. aspera* seed epicotyls layer extract

The fresh *A. aspera* Linn seeds were collected from the surroundings of the Vellore district, Tamilnadu, India. The seed epicotyls layer extract is used for the reduction of  $\text{Au}^{3+}$  ions to AuNPs. 1 g of finely ground and meshed *A. aspera* seed powder was mixed with 100ml of de-ionized water and heated at  $90^\circ\text{C}$  in a temperature controlled water bath for about 1 hr and cooled, and then passed through a  $0.2 \mu\text{m}$  cellulose nitrate membrane filter paper.

### b) Synthesis of AuNPs

The aqueous seed epicotyls layer extract of 200  $\mu\text{l}$  of *A. aspera* Linn was added to 2ml of 0.01 M  $\text{HAuCl}_4$  solution and mixed thoroughly by manual shaking. Formation of AuNPs was instantaneous and observed as a visual color change from yellow to pink-ish red [9].

Green synthesis of gold nanoparticles from the fruit extract of *Terminalia arjuna*, for the enhanced seed germination activity of *Gloriosa superba*.

### a) Synthesis of Au NPs using *T. arjuna* fruit extract

Fresh *T. arjuna* fruits were cleaned in running tap water and then by distilled water. 10g of fruits were added with 100ml of double-distilled water and boiled at 50–60°C for 5 mins. The obtained extraction was filtered using Whatman No. 1 filter paper, while the filtrate was collected in a 250ml Erlenmeyer flask, and then stored at room temperature for further usage. Thereafter, 1ml of *T. arjuna* fruit extract was added to 100ml of 1 mM  $\text{HAuCl}_4$  solution at room temperature and the reduction of Au NPs was clearly observed within the next 15 min period [10].

Biogenic synthesis of Ag, Au and bimetallic Au/Ag alloy nanoparticles using the aqueous extract of mahogany (*Swietenia mahogani* JACQ.) leaves.

### a) Preparation of aqueous extracts of leaves of mahogany

1g of the dried leaves of mahogany was boiled with 15ml of double-distilled water at 100°C for 5 mins. After that, the solution was filtered and the filtrate was obtained as a clean brown solution that was used for the biogenic synthesis of Au and Ag nanoparticles, as well as bimetallic Au/Ag nanoparticles.

### b) Method of synthesis of Ag, Au and bimetallic Au/Ag alloy nanoparticles

Metal nanoparticles were synthesized by adding the aqueous solution of  $\text{AgNO}_3$  or  $\text{HAuCl}_4$  to the aqueous extract of mahogany. In the case of Ag nanoparticle synthesis, 60 $\mu\text{L}$  of leaf extract of mahogany was added to 5ml of double-distilled water followed by stirring for 2 mins. To this solution, 30 $\mu\text{L}$  of 0.05M  $\text{AgNO}_3$  solution was added so that the final concentration of AgI ions became  $3 \times 10^{-4}$  M. The reaction mixture was then continuously stirred at  $\sim 40$  °C. Within 30 mins, a yellow coloration

appeared, indicating the onset of Ag nanoparticle formation. The progress of the reaction was monitored by measuring the absorbance of the solution at regular intervals of time. The same procedure has been repeated at two different pH levels: 8.5 and 12.5, respectively. For the solutions at pH 12.5, upon stirring at room temperature for 5 mins, a prominent peak appears at 438 nm. Upon stirring at room temperature for 25 mins, a prominent peak appears at 422 nm for the solution at pH 8.5. For Au nanoparticle synthesis, a similar method has been followed, except that 50 L of 0.01 M aqueous HAuCl<sub>4</sub> solution was used instead of AgNO<sub>3</sub> aqueous solution. In this case, the final concentration of Au<sup>III</sup> ions becomes  $1 \times 10^{-4}$  M. Within 5 mins a pink coloration was observed which indicated the onset of Au nanoparticle formation [11].

Biogenic synthesis of Au and Ag nanoparticles using aqueous solutions of Black Tea leaf extracts.

a) Preparation of leaf extract

The method of preparation was as follows. For the tea leaf broth, 180 g of dried tea leaves were boiled in 400 ml water. The resulting infusion was then filtered thoroughly and repeatedly until no insoluble material appeared, giving the tea leaf broth. A portion of the broth was set aside for nanoparticle preparation. From the remaining portion, the CH<sub>2</sub>Cl<sub>2</sub> and ethyl acetate soluble parts were isolated in the form of solid masses. Both of these solids were moderately soluble in water so that their aqueous solutions were prepared as CH<sub>2</sub>Cl<sub>2</sub> extract and ethyl acetate extract, respectively, and used in the synthesis of Ag and Au nanoparticles.

b) Synthesis of AgNO<sub>3</sub> or HAuCl<sub>4</sub>

Metal nanoparticles were synthesized by adding aqueous solutions of AgNO<sub>3</sub> or HAuCl<sub>4</sub> to any of the three solutions: tea leaf Scheme used for the preparation of the tea leaf extracts used for metal nanoparticle synthesis. Broth, ethyl acetate extract or CH<sub>2</sub>Cl<sub>2</sub> extract. In a typical synthesis, 75 L of 0.01 M AgNO<sub>3</sub> was added to 10 ml of any of the solutions with continuous stirring, at  $\sim 40$  °C. Within 30 mins a yellow coloration appeared, indicating the onset of Ag nanoparticle formation. The progress of the reaction was monitored by measuring the absorbance of the solution at regular intervals of time. For Au nanoparticles, a similar method was followed, except that 75 L of 0.01 M HAuCl<sub>4</sub> was used instead of AgNO<sub>3</sub>. Thus, the final metal ion concentration in both cases was  $7.5 \times 10^{-5}$  M. Absorption spectra were measured on a Shimadzu UVPC-3200

spectrophotometer. Samples for transmission electron microscopy (TEM) were prepared by drop-coating the Ag and Au nanoparticle solutions onto carbon-coated copper grids. The films on the grids were allowed to dry prior to TEM measurement in a JEOL TEM-2010 instrument. [12].

Plant-mediated synthesis of silver and gold nanoparticles and their applications.

#### a) Synthesis of Gold

A very simple procedure was followed in the synthesis of gold nanoparticles using geranium (*Pelargonium graveolens*) leaf extract. Leaves were finely cut and boiled in water. A small quantity of leaf broth was inoculated with an aqueous solution of 1 mmol L<sup>-1</sup> chloroauric acid (HAuCl<sub>4</sub>) and allowed to react for 2 hrs. This short exposure of leaf broth with aqueous chloroaurate ions caused a rapid reduction of the metal ions leading to the formation of stable gold nanoparticles of variable size and shapes such as rods, flat sheets and triangles [63, 64].

#### b) Synthesis of Silver

In silver nanoparticles synthesized by treating silver ions with Capsicum annum L. extract, the crystalline phase of the nanoparticles changed from polycrystalline to single crystalline and their size increased with increasing reaction time. 5 hrs reaction time led to spherical and polycrystalline shaped nanoparticles (10±2 nm). With an increase in reaction time to 9 hrs and 13 hrs, the size of the nanoparticles was increased to 25±3 nm and 40±5 nm, respectively. Identifying the responsible molecules involved in the synthesis of nanoparticles, about 3 nm protein moieties have been found to be capping the silver nanoparticles [13].

Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf.

#### a) Preparation of dried biomass

*Cinnamomum camphora* trees were cultivated by Xiamen Peony Perfume & Chemicals Industry Co. Ltd, China. The freshly harvested *C. camphora* leaves were exposed to the sun until they were completely dried. The biomass used for the reduction was prepared by crushing the dried leaves and then screening the leaf powder by a 20 mesh sieve.

b) Synthesis for silver and gold nanoparticles

Two chemicals, silver nitrate ( $\text{AgNO}_3$ ) and chloroauric acid ( $\text{HAuCl}_4$ ), were purchased from Sinopharm Chemical Reagent Co. Ltd, China and were used as received. In a typical synthesis for silver and gold nanoparticles using dried powder of *C. camphora* leaf, the carefully weighted biomass was added to 50ml of 1 mM aqueous  $\text{AgNO}_3$  and  $\text{HAuCl}_4$  solution, respectively, in conical flasks of 100ml content at room temperature. The flasks were thereafter shaken at a rotation rate of 150rpm in the dark at 30°C [14].

Green synthesis of silver and gold nanoparticles using flower bud broth of *Couropita guinensis* Aublet.

a) Preparation of extract

The collected flower buds were thoroughly washed with tap water followed by distilled water to remove the surface contaminants and partially dried for 24 hrs in the shade. The partially dried flower buds were ground to make a paste using mortar and pestle without adding any solvent. 10g of the flower bud paste was added to 100ml of distilled water and boiled at 70-80°C for 10 mins to prepare the flower bud broth [65, 66].

b) Synthesis of silver and gold nanoparticles

10ml of freshly prepared flower bud broth was quickly resuspended in 90ml of an aqueous solution of silver nitrate. 10ml of freshly prepared flower bud broth was quickly added to 90ml of an aqueous solution of gold chloride for the bioreduction of gold ions in to gold nanoparticles [67, 68]. These suspensions were kept in an incubator cum shaker (OrbitekModel) with 150 rpm at 36°C for 24 hrs. From each of these reaction media a small aliquot of the sample was taken after the centrifugation and used to characterize the silver and gold nanoparticles that were synthesized in their respective reaction media. The characterization was performed through the following analyses: UV-Vis, FT-IR, XRD, SEM, EDX and TEM. [15].

Brown Algae mediated synthesis, characterization of gold nanoparticles using *Padina pavonica* and their antibacterial activity against human pathogens.

a) Preparation of algal thallus

Collected algae *Padina pavonica* were washed thoroughly with tap water to remove both epiphytes and necrotic plants, and then rinsed with sterile distilled water to remove any debris. The fresh materials were shade dried for one week and finely powdered using a domestic blender and sieved to mesh <0.5mm. For the algae thallus broth preparation, 10g of algae powder was heated at 70°C with 100ml de-ionized sterile distilled water for 20 mins. The resulting infusion was filtered thoroughly using Whatman filter paper No. 1 until no insoluble material appeared in the algae extract.

b) Synthesis of gold nanoparticles

75ml (15%) of algae extract was added to 425ml of de-ionized sterile distilled water. 0.19g of  $10^{-3}$  M chloroauric acid was added to the above solution and incubated at room temperature for reduction of Au<sup>+</sup> ions. After 2 hrs of reaction, color change was observed from brown to dark purple due to the excitation of surface plasmon vibrations in the gold metal nanoparticles. The reduction of pure Au<sup>+</sup> ions was monitored by measuring the UV-vis spectra of the solution after 24 hrs and 48 hrs of reaction. The surface plasmon band occurred at 545.5 and 542.5 after 24 hrs and 48 hrs of reaction respectively [16].

c) Purification of gold nanoparticles

The broth containing the nanoparticles was centrifuged at 5,000 rpm for 15 mins at 27°C three times to obtain the dry powder of the gold nanoparticles, following which the pellet was re-dispersed in sterile distilled water to remove any biological molecules. The process of centrifugation and re-dispersion in sterile de-ionized distilled water was repeated three times to obtain better separation of the entities from the metal nanoparticles. The purified pellets were then freeze-dried using a lyophilizer [16].

The Synthesis of gold nanoparticles using *Amaranthus spinosus* leaf extract and the study of their optical properties\*.

a) Preparation of extract and synthesis of gold nanoparticles

The collected leaves were washed with double-distilled water and shadow dried before being ground to a fine powder and sieved to remove coarse particles. 1g of leaf powder was mixed with 100ml of ethanol and the



mixture was left in a shaking incubator operating at 200 rpm, at 25°C for 24 hrs. The extract was then filtered and the filtrate was used for AuNPs synthesis. Various concentrations (1% - 5%, v/v) of the ethanolic leaf extract of *A. spinosus* were mixed with an aqueous solution of HAuCl<sub>4</sub> (1 mM) and the reaction volume was made up to 2ml with distilled water. The mixture solution was left on constant magnetic stirring at room temperature (25°C) and observed for change in color [17].

Green synthesis of gold nanoparticles from *Cassia auriculata* leaf aqueous extract and its cytotoxicity effect on *in vitro* cell line.

a) Preparation of aqueous extracts

The fresh and healthy leaves were collected and washed with distilled water to remove dust particles. After washing the leaves, they were spread evenly on clean paper and the leaves were allowed to dry in the shade for 3-4 days. When the leaves were dried completely they were finely powdered using a food mixer and then used for extract preparation. About 2g of each leaf sample was mixed with 50ml of glass-distilled water and the mixture was boiled at 60°C for 20 mins. The mixture was brought to the room temperature and the aqueous leaf extract was collected using Whatman filter paper. It was stored in a glass bottle and kept under refrigeration for future use.

b) Synthesis of gold nanoparticles

1ml of aqueous leaf extract was taken and 1mM HAuCl<sub>4</sub> was added and the reaction volume was made up to 10ml by adding glass-distilled water. The solution was observed for color change from yellow to ruby red within 1 hr, indicating the synthesis of gold nanoparticles. The control solution was maintained for all six extracts without adding HAuCl<sub>4</sub>. The color change from yellow to ruby red was observed in aqueous extracts of *Cassia auriculata* within 10 mins. This is now available for further study. [18].

Biosynthesis of Au nanoparticles by *Gymnocladus assamicus* and its catalytic activity

a) Preparation of extract and synthesis of gold nanoparticles

2ml of *G. assamicus* pod extract was added to 10ml of 10<sup>-3</sup> M aqueous HAuCl<sub>4</sub> solution for the synthesis of the Au nanoparticles. The solutions were then subject to continuous stirring at 30°C for 4 hrs. The ruby red

color of the reaction mixture visually indicates the formation of Au nanoparticles. Preliminary characterization of the formation of nanoparticles was monitored by UV/vis spectroscopy. UV/vis spectra were recorded in the range between 200 and 900 nm using a UV/vis spectrophotometer (Model: Lamda25, Switzerland). X-ray diffraction (XRD) measurement was carried out in a Rigaku X-ray Diffractometer (Model: ULTIMAIV, Rigaku, Japan) with Cu-K $\alpha$  X-ray source ( $\lambda$ 1.54056Å) at a generator voltage of 40kV. The high-resolution transmission electron microscopy (HRTEM) images were taken by a JEOL Model 2100EX instrument operated at an accelerating voltage of 200kV. Samples for HR TEM imaging were prepared by placing a drop of the solution sample in de-ionized water and then on to a carbon-coated Cu grid. In HPLC analysis the separation was accomplished on a Shimadzu Prominence HPLC instrument equipped with a manual injection, a programmable wavelength photodiode array (PDA) UVdetector (200–400nm) and a column packing with modified silicagel (C18 column).

#### b) Catalytic activity

To study the catalytic activity of prepared Au nanoparticles, the reduction of 4-nitrophenol to 4-aminophenol by NaBH<sub>4</sub> is performed as a probe reaction. The effect of the concentrated Au solution on the speed of catalytic reduction was studied by using different quantities (100, 200, 300, 400 and 500  $\mu$ l) of Au colloids [19].

Catalytic reduction of methylene blue using biogenic gold nanoparticles from *Sesbania grandiflora* L

#### a) Preparation of leaf extract

Aqueous extract of *S. grandiflora* was prepared using freshly collected leaves (10g). They were surface cleaned with running tapwater, followed by being ground with 100ml of sterilized Milli Q water using mortar and pestle. The resulting extract was filtered through Whatman no.1 filter paper and used for further assays.

#### b) Synthesis of gold nanoparticles

For the synthesis of AuNPs, varying amounts (0.065–2.0ml) of *S. grandiflora* leaf extract were added separately to the 8ml of 1 mM aqueous gold solution (HAuCl<sub>4</sub>·4H<sub>2</sub>O). The final volume of salt and leaf extract solution was increased to 10ml by adding an appropriate amount of Milli Q water. This reaction mixture was then heated at 60°C, and the solution

became ruby red in color after 3 mins. UV–vis spectra showed strong SPR band at 534 nm, thus indicating the formation of AuNPs. The AuNPs solution thus obtained was purified by repeated centrifugation at 18,000 rpm for 35 mins followed by re-dispersion of the pellet in Milli Q water. It is characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

c) Evaluation of the reduction of methylene blue by biogenic AuNPs

In order to investigate the reduction of MB by *S. grandiflora* extract in the presence of gold nanocatalyst, the suspension of AuNPs were coated onto the surface of borosilicate glass beads and dried at 120°C for 2 hrs. The catalytic reduction reaction was carried out in a standard quartz cell with a 1cm path length and about 3ml volume. The procedure entailed the mixing of 0.25ml of plant extract with 3ml of MB ( $1 \times 10^{-4}$  M) solution in the quartz cell in the presence and absence of glass beads coated with AuNPs. The absorption spectra of the reaction solutions (1.0ml) were recorded at room temperature using Perkin-Elmer double beam spectrophotometer in the range of 250–50 nm. The rate constant of the reduction process was determined by measuring the change in absorbance at 614 nm as a function of time [20].

Controllable biosynthesis of gold nanoparticles from a *Eucommialmoides* bark aqueous extract

a) Preparation of *E. ulmoides* aqueous extract

The naturally available *E. ulmoides* bark was thoroughly washed and cleaned using super-purified water, and powdered after being dried at room temperature. 20g of the bark powder in 100ml of purified water was boiled in a water bath at 80°C for 30 mins. The mixtures were filtered, sequentially the filter liquor was centrifuged at 15,000 rpm for 10 mins. The aqueous extract was stored in the refrigerator at 4°C for further studies.

b) Green synthesis of Au nanoparticles

All glassware used was thoroughly cleaned using detergent and aqua regia solution (HCl–HNO<sub>3</sub>, 3:1) for the complete removal of potential artificial nucleation sites. A mount of 1 mM aqueous solution of chloroauric acid (HAuCl<sub>4</sub>) was mixed with varying quantities (1ml, 2ml, 3ml, 4ml, 5ml and

6ml) of *E. ulmoides* aqueous extract in a 10ml flask. After adjusting the solution pH using 0.1 M NaOH, the sealed flask was incubated in the water bath at a constant temperature for several mins. The colloidal solution was cooled at room temperature, transferred to a plastic tube and stored at room temperature. AuNPs exhibit surface plasmon resonance at 530–550 nm. Synthesized gold nanoparticles characterized by UV-visible spectroscopy, high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), reflection absorption – fourier transform infrared (RA-FTIR) and zeta potential measurement and particle size analysis.

c) Evaluation of catalytic activity

100  $\mu$ L as-synthesized AuNPs colloid solution and 100  $\mu$ L NaBH<sub>4</sub> (0.2 M) were added sequentially into 3ml of the azo-dyesolution (30mg/L) with. The UV–vis spectra of the solution were scanned at room temperature in a range of 300–700 nm using quartz cell (1cm path length) and the absorbance was determined at the maximum absorption wavelength of the reactive yellow 179 or Congo red. The change of absorbance was used as a criterion to evaluate the reduction efficiency [21].

Nerium oleander leaves extract mediated synthesis of gold nanoparticles and its antioxidant activity

a) Preparation of leaf extract

Nerium oleander leaves were collected from Lakki Marwat KP, Pakistan, and shade dried for four days, and then ground into fine powders. Then 10g of it was mixed with 100ml of water and stirred at 60°C for 5 hrs and then filtered to get the aqueous extract.

b) Synthesis of gold nanoparticles

For gold nanoparticles synthesis, 10ml of Nerium oleander leaf extract was added with continuous stirring to 50ml of  $3 \times 10^{-2}$  M aqueous solution of HAuCl<sub>4</sub> in a 150ml beaker. As a visual observation, color change occurs from yellow to black within 2 hrs. The appearance of black color confirmed the formation of gold nanoparticles. The biogenic gold nanoparticles were characterized by scanning the aliquot sample in the wavelength range of 200–800 nm and recorded the absorption maxima in Shimadzo UV-24003 spectrophotometer at a resolution of 1 nm. The wide-angle X-ray diffraction (XRD) measurements were carried out on a Rigaku D/Max 2500 VBZ+/PC diffractometer using Cu K <sub>$\alpha$</sub>  radiations at a

scanning rate of 20 min<sup>-1</sup> with an operating voltage of 40kV and a current of 200mA. High-resolution transmission electron microscopy (HRTEM) on a JEM-3010 microscope with an accelerating voltage of 200kV was used to examine the morphologies and size of the nanoparticles. Infrared (IR) spectrum of Nerium oleander leaf extracts was obtained using the KBr pellet technique on an ABB MB3000 spectrophotometer where it was scanned between 2000 and 500 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> in transmittance mode [22].

Phytofabrication of gold nanoparticles assisted by leaves of Suaeda monoica and its free radical scavenging property

a) Collection and preparation of leaf extract

The leaves of *S. monoica* were collected from the coastal region of Vellar estuary, Parangipettai (Lat 11°29'N; Long 79°46'E), south east coast of India. They were brought to the laboratory in an icebox, washed in distilled water and subsequently shade dried for a week. Then they were kept in an oven at 60°C until a constant weight was obtained. The dried leaves were ground to a powder and sieved through <0.5mm.

b) Synthesis of gold nanoparticles

Aqueous solution (1 mM) of hydrogen tetrachloroaurate (HAuCl<sub>4</sub>) was prepared and used for the synthesis of gold nanoparticles. Briefly, 250mg of *S. monoica* biomass was added to 10ml of HAuCl<sub>4</sub> solution and incubated in a hot air oven. The reduction of metal ions was roughly monitored by visual observation of the solution. Synthesized gold nanoparticles were confirmed by UV-visible spectroscopy (Perkin Elmer Lambda 25) by sampling the aqueous component (2ml), diluted to 20 times and measuring the UV-vis spectra of the solution. Dry powder of gold nanoparticles was obtained in the following manner: after the desired reaction period, the biomass of *S. monoica*-HAuCl<sub>4</sub> mixture solution containing the gold nanoparticles was centrifuged at 12,000 rpm for 15 mins. The pellets were redispersed in Millipore water to remove any uninteracted biological molecules. This process of centrifugation was repeated three times to ensure better separation of the gold nanoparticles. The purified pellets were then freeze-dried and lyophilized. The purified dried powder was then used for the subsequent characterization studies which included: scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), dynamic light scattering (DLS) and fourier transform infrared spectroscopy (FTIR).

c) 1,1-Diphenyl-2-picrylhydrazyl (DPPH) radical quenching assay

The free radical scavenging capacity of gold nanoparticles was determined using 1,1-diphenyl-2-picrylhydrazyl (DPPH) [69]. The reaction mixture was incubated at 37°C for 30 mins and the color change was measured spectrophotometrically at 517 nm. The percentage of DPPH scavenging activity was calculated by DPPH radical scavenging activity (%) =  $[(A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}] \times 100$ . Where  $A_{\text{control}}$  is the absorbance of the control reaction and  $A_{\text{sample}}$  is the absorbance in the presence of AuNPs by S. Monoica [23].

Phytochemical mediated gold nanoparticles and their PTP 1B inhibitory activity

a) Preparation of extract and synthesis of gold nanoparticles using guavanoic acid

1g of dried biomass of Pg leaf was dissolved in 100ml of 1×10<sup>-3</sup>M aqueous AuCl<sub>4</sub>-solution. Bioreduction of AuCl<sub>4</sub>-was monitored by recording UV-vis spectra (Schimadzu 1600) for the above reaction mixture on solution-cast films of gold nanoparticles on a quartz substrate and operates at a resolution of 1 nm. In order to characterize the compound responsible for the reduction and capping of AuCl<sub>4</sub>- the leaf biomass (800g) of Pg was extracted with methanol, chloroform, ethyl acetate, acetone, petroleum ether and hexane in soxhlet apparatus separately until exhaustion. The extractions were dried, weighed and tested for reaction with aqueous chloroauric acid. The methanolic extract which indicates its bioreduction property of H<sub>2</sub>AuCl<sub>4</sub> was further separated into seven fractions by column chromatography using (60–120 mesh) a glass column 2.5cm and length 30cm as stationary phase and methanol: chloroform:hexane gradient as the eluting system. Each fraction was tested for bioreduction property of H<sub>2</sub>AuCl<sub>4</sub>. The fraction which indicates its bioreduction property was subjected to a subsequent repeated column chromatography using different Si gel mesh (100–200 mesh) with varying proportions of methanol:chloroform:hexane as eluents to collect different subfractions and were tested. All fractions were monitored TLC (pre-coated plate 0.02mm thick E-merck Germany) until a single spot was obtained. The fraction that exhibits the bioreduction property was carefully evaporated to dryness and subsequently characterized by UV-vis spectra, FTIR, NMR and GC-mass analysis as guavanoic acid. 1ml of 5mg of guavanoic acid was added into 49ml of 1×10<sup>-3</sup>M aqueous chloroaurate solution. The color of the reaction solution turned from pale yellow to

ruby red color within 1 min of reaction, which indicates the rapid formation of gold nanoparticles [24].

Spontaneous ultra-fast synthesis of gold nanoparticles using *Punica granatum* for cancer targeted drug delivery

a) Preparation of extract and synthesis of gold nanoparticles

125  $\mu$ l of plant extract (60g/100ml H<sub>2</sub>O) was mixed with 10ml of  $1 \times 10^{-3}$ M gold solutions. It was observed that the yellow colored gold solution turned to wine red color within 1 min. The yield of gold nanoparticles was optimized by changing the pH of the aqueous solution, volume of gold solution and extract required to reduce the gold solution to nanoparticles. Preliminary characterization of PAuNPs was carried out by UV-vis spectroscopy, FTIR, TEM and particle size analysis method [25].

Biosynthesis of gold nanoparticles using *Solanum nigrum* leaf extract and screening their free radical scavenging and antibacterial properties

a) Preparation of leaf extract

The fresh and healthy leaves of *S. nigrum* were washed several times with de-ionized water until no foreign material remained. 10g of leaf was finely cut and stirred with 100ml of de-ionized water at 85°C for 20 mins. The leaf extract was filtered with Whatman no.1 filter paper and the filtrate was stored at 4°C for further experiments as reducing agent and stabilizer, being usable for within 2 weeks.

b) Biosynthesis of gold nanoparticles

The synthesis of gold nanoparticles involved the mixing of aliquot amounts of chloroauric acid and *S. nigrum* leaf extract in water. The *S. nigrum* leaf extract (0.2, 0.4, 0.6, 0.8 and 1ml) was added to 10ml of 1 mM HAuCl<sub>4</sub> aqueous boiled solution and kept at boiling condition for 20 mins to get the colloids g<sub>1</sub>, g<sub>2</sub>, g<sub>3</sub>, g<sub>4</sub> and g<sub>5</sub>, respectively. The formation of nanoparticles was indicated by a visual color change from pale yellow to violet and then to a purple pink color. The reduction was observed to be slow at lower concentrations of leaf extract. The reduction rate was found to increase with an increase in the quantity of the leaf extract. For g<sub>5</sub>, fast reduction occurred as indicated by violet to purple pink color of the solution, and the reaction rate was completed after 24 hrs. Synthesized gold nanoparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction

(XRD), particle size analyser, Zeta potential measurement and fourier transform infrared spectroscopy (FTIR).

c) Free radical scavenging activity

1,1-diphenyl-2-picrylhydrazyl (DPPH) radical assay biosynthesized Au-NPs and *S. nigrum* were tested for the scavenging effect on DPPH radical according to the method of Blois [29]. Different concentrations (50L, 100L and 150 L) of *S. nigrum* and biosynthesized AuNPs were added, in equal volume, to 0.1 mM methanolic DPPH solution. The reaction mixture was incubated for 30 mins at room temperature under shaking conditions and the absorbance was recorded at 517 nm. The synthetic antioxidant butyl hydroxyl toluene (BHT) was used as positive control. All determinations were performed in triplicate. The DPPH radical scavenging activity (RSA) was expressed as a percentage of inhibition using the following formula.

$$\% \text{ RSA} = [\text{A}_{\text{control}} - \text{A}_{\text{sample}} / \text{A}_{\text{control}}] \times 100$$

Where,  $\text{A}_{\text{sample}}$  is the absorbance of the blank control and  $\text{A}_{\text{control}}$  is the absorbance of the test sample.

Hydroxyl radical scavenging assay Hydroxyl radicals were generated by a Fenton reaction system ( $\text{Fe}^{3+}$ - ascorbate - EDTA  $\text{H}_2\text{O}_2$ ) and the scavenging capacity towards the hydroxyl radical was measured by using a deoxyribose method (Halliwell) [30]. The reaction mixture contained 0.8ml of phosphate buffer solution (50 mmol  $\text{L}^{-1}$ , pH 7.4), 0.2ml of a sample of different concentrations (50L, 100L and 150  $\mu\text{L}$ ), 0.2ml of EDTA (1.04 mmol  $\text{L}^{-1}$ ), 0.2ml of  $\text{FeCl}_3$  (1 mmol  $\text{L}^{-1}$ ), and 0.2ml of 2-deoxyribose (60 mmol  $\text{L}^{-1}$ ). The mixtures were kept in a water bath at 37°C and the reaction was started by adding 0.2ml of ascorbic acid (2 mmol  $\text{L}^{-1}$ ) and 0.2ml of  $\text{H}_2\text{O}_2$  (10 mmol  $\text{L}^{-1}$ ). After incubation at 37°C for 1 hr, 2ml of cold thiobarbituric acid (10 g  $\text{L}^{-1}$ ) was added to the reaction mixture followed by 2ml of HCl (25%). The mixture was heated at 100°C for 15 mins and then cooled down with water. The absorbance of the solution was measured at 532 nm with a spectrophotometer. The hydroxyl radicals scavenging capacity were evaluated with the inhibition percentage of 2deoxyribose oxidation on hydroxyl radicals. The scavenging percentage was calculated according to the following formula.

$$\% \text{ Scavenging} = [\text{A}_0 - (\text{A}_1 - \text{A}_2)] \times 100/\text{A}_0$$



Where  $A_0$  is the absorbance of the control without a sample,  $A_1$  is the absorbance after adding the sample and deoxyribose and  $A_2$  is the of the sample without deoxyribose [26].

Antibacterial activities of *Hibiscus cannabinus* stem-assisted silver and gold nanoparticles

a) Preparation of extract and synthesis of gold nanoparticles

An aqueous solution of  $\text{HAuCl}_4$  was added to 5ml of stem extract and stirred for 5 mins at room temperature. During the synthesis it initially became colorless and turned into purple, indicating the formation of AuNPs. Similarly, an aqueous solution of  $\text{AgNO}_3$  (3 mM) was added to 5ml of fruit extract and stirred for 5 mins at room temperature. With the addition of the extract, the colorless solution changes color from light yellow to reddish orange indicating the formation of AgNPs. The absorption spectra of the prepared NPs were measured using a Shimadzu spectrophotometer (UV1700). XRD analysis of the NPs was done using PANalytical X'pert – PRO Diffractometer with  $\text{CuK}\alpha$  radiation operated at 40kV/30mA. FTIR measurements were obtained on a Nexus670 FTIR instrument with the sample as KBr pellets. TEM analysis was done using a JEOLJEM2100 HRTEM operating at 200kV. A disc diffusion method was used to evaluate the antibacterial action of prepared NPs against bacteria, namely *Pseudomonas aeruginosa* (gramnegative) and *Staphylococcus aureus* (Gram positive) [27].

Green synthesis, characterization and antimicrobial activity of Au NPs using *Euphorbia hirta* L. leaf extract

a) Synthesis of gold nanoparticles

Fresh leaves of *E. hirta*, were washed several times with ultra pure water to remove dust. The leaf extract used was prepared from 5g of thoroughly washed leaves and heated in 50ml of ultra-pure water for 5 mins in an Erlenmayer flask using a water bath. The filtered leaf extract was stored at  $-15^\circ\text{C}$  for further use, being usable for 1 week. Synthesized gold nanoparticles characterized by UV-visible spectrophotometer, particle size analyser, energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) [28].

Green synthesis of gold nanoparticles using seed aqueous extract of *Abelmoschus esculentus* and its antifungal activity

a) A. esculentus seed powder preparation

The obtained seeds were washed thoroughly in tap water and finally rinsed with distilled water until no foreign material remained. The freshly cleaned seeds were left to dry for 15 days at room temperature. The dried seeds were pulverized with a sterile electrical blender to obtain a powdered form. The powdered samples were stored in an air-tight container and protected from sunlight for further use.

b) A. esculentus seed aqueous broth preparation and synthesis of Au NPs

2g of finely powdered seed was mixed with 100ml of de-ionized water and then the mixture was boiled for 30 mins, cooled and filtered through Whatman No. 1 filter paper. The extract was used fresh within 1hr. 40ml of A. esculentus seed aqueous broth was added to 60ml of 1 mM aqueous HAuCl<sub>4</sub> solution and the solution was placed in an orbital shaker at room temperature for the reduction of Au<sup>3+</sup> to Au<sup>0</sup>. The bio-reduction of the gold ions in the solution was monitored periodically by measuring the UV-visible spectroscopy of the solutions. The reaction was rapid as the ruby red color appeared within 10 mins and the reaction confirmed the formation of Au NPs, and there was no further color change. The control seed aqueous broth of A. esculentus without auric chloride did not show any change in color. The optimum time required for the completion of the reaction was 10 mins. A different concentration of HAuCl<sub>4</sub> solution was used to get maximum Au NPs. The overall optimized reaction condition was observed in a 1 mM HAuCl<sub>4</sub> solution and neutral pH. The Au NPs obtained from the solution were purified by repeated centrifugation at 2000 rpm for 10 mins followed by dispersion of the pellet three times in de-ionized water to remove the water-soluble biomolecules, such as proteins and secondary metabolites. The water suspended NPs were frozen at 30°C overnight and then kept under vacuum for 24 hrs to dry the NPs. Different instrumental techniques were used for the characterization, such as FESEM, UV-visible spectrophotometer, X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) [29].

Barbated Skullcup herb extract-mediated biosynthesis of gold nanoparticles and its primary application in electrochemistry

a) Preparation of extract and synthesis of gold nanoparticles

The BS herb extract used for the reduction of gold ions and the synthesis of gold nanoparticles was prepared by taking 1g of BS herb powder in a 100ml Erlenmeyer flask with 30ml of distilled water and incubating it at room temperature for 3 hrs. The solution was then decanted and filtered. The effect of HAuCl<sub>4</sub> concentration in the mixed solution on the biosynthesis of gold nanoparticles was investigated first. The different concentrations of HAuCl<sub>4</sub> in the mixed solution were produced by adding to its volume. Different volumes (0.2–2.0ml) of the HAuCl<sub>4</sub> solution (0.01M) were added to the extract solution. And all the experiments were duplicated at least five times. After mixing the BS herb extract with aqueous HAuCl<sub>4</sub> the solution changed to pink rapidly, indicating a reduction of gold ions to yield gold nanoparticles. The kinetics of the reduction was monitored by measuring the UV–vis spectra of the solution. Allowing the reduction of gold ions in the reaction mixtures had saturated, samples of BS herb reduced gold nanoparticles were centrifuged at 1500 rpm for 10 mins, and the pellet obtained was washed with de-ionized water to remove any possible biomass. The collected products were characterized using UV–vis spectroscopy, transmission electron microscopic (TEM), and energy dispersive X-ray spectrometer (EDX) element analysis. UV–vis absorption spectra were measured on a Beckman DU-800 UV–vis spectrophotometer. The morphologies of gold nanoparticles were characterized by JEOL-1230 TEM analysis. Samples were prepared by drop coating gold nanoparticles solutions onto carbon coated copper TEM grids and dried at room temperature. TEM measurements were performed on an instrument and operated at an accelerating voltage at 100kV. Additionally, the particle size distribution of the gold nanoparticles was determined by dynamic light scattering (Zetasizer3000 HSA, Malvern, UK). Element analysis was carried out using EDX (IXRF Systems Inc., TX).

b) Preparation of biosynthesized gold nanoparticles modified electrode

The electrode modified with biosynthesized gold nanoparticles film was prepared by a simple casting method. Briefly, 20L of the biosynthesized gold nanoparticles solution was cast onto the surface of the freshly polished GCE. A small beaker was covered over the electrode to serve as evaporating room so that the films dried gradually in air, allowing a uniform film to be formed. The final electrode was denoted as biosynthesized gold nanoparticles GCE (biogenic/AuNPs GCE).

### c) Electrochemistry catalytic function measurement

The biosynthesized gold nanoparticles modified electrode was used to detect the electrocatalytic reductions of p-nitrophenol. Electrochemical experiments were performed on a CHI600 electrochemistry station. The standard three-electrode system was used for the measurements with a platinum electrode as counter electrode, an Hg/HgCl<sub>2</sub> (KCl-saturated) electrode as reference electrode with respect to which all potentials were reported and a GCE as working electrode. The 10<sup>-3</sup> M phosphate buffer solution (PBS) used as electrolytes was purged with purified nitrogen for at least 20 mins to remove oxygen and nitrogen atmosphere environment was kept during electrochemical measurements. Unless stated, the experiments were under taken at ambient condition with temperature of 25±3 °C [30].

## 2. Palladium

Rapid green synthesis of palladium nanoparticles using the dried leaf of *Anacardium occidentale*.

### a) Preparation of leaf powder

Fresh *A. occidentale* leaves were collected, washed with DM water and air dried for two weeks. It is then finely powdered and stored. The precursor, PdCl<sub>2</sub> for the preparation of Pd NPs was purchased from Sigma Aldrich.

### b) Synthesis of gold nanoparticles

To prepare the palladium nanoparticles, 300mg of leaf powder was added to 30ml of 1.7 × 10<sup>-4</sup> M aqueous PdCl<sub>2</sub> solution with constant stirring at 80°C. The reduction occurred rapidly which is indicated by the color change of the solution from light to bright brown color. The Pd colloid thus formed is stable at room temperature for 1 month [31].

Biogenic synthesis of palladium nanoparticles using *Pulicaria glutinosa* extract and their catalytic activity towards the Suzuki coupling reaction.

### a) Preparation of extract

PdCl<sub>2</sub> (99.9%), bromobenzene (99.5%), sodium dodecyl sulphate (98%), phenyl boronic acid (95%), tripotassium phosphate (98%) and other solvents were purchased from Sigma Aldrich and were used without any further purification. The plant specimen of wild growing *P. glutinosa* was

collected from the hilly areas of Al-Hair in central Saudi Arabia during March 2011. The identity of the plant material was confirmed by a plant taxonomist from the Herbarium Division of the College of Science, King Saud University, Riyadh, Kingdom of Saudi Arabia. A voucher specimen was deposited in our laboratory as well as in the Herbarium Division of King Saud University with the voucher specimen number KSU21598. The details of the preparation of plant extract were given in our previous study.<sup>45</sup> The solution of the plant extract used for the reduction of PdCl<sub>2</sub> was prepared using 0.1 g of plant extract in 1 ml of solvent.

b) Synthesis of palladium nanoparticles

In a typical experiment, the reaction mixture was prepared by adding 5 ml of the plant extracts to 95 ml of 1 mM PdCl<sub>2</sub> (177.33 mg) solution in a 150 ml round bottom flask, mounted with a cooling condenser and a magnetic stir bar. The mixture was stirred for 2 hrs at 90°C (an immediate color change was observed from light yellow to dark brown; no further color change was observed after 2 hrs). After 2 hrs the mixture was allowed to cool down, followed by centrifugation (9000 rpm). After washing three times with distilled water, a black powder was obtained which was dried overnight in an oven at 80°C.

c) Suzuki reaction catalyzed by Pd nanoparticles

A mixture of sodium dodecyl sulfate (144 mg, 0.5 mmol), tri potassium phosphate (K<sub>3</sub>PO<sub>4</sub>, 399 mg), phenylboronic acid (146 mg, 1.2 mmol) and de-ionized water (20 ml) was placed in a 100 ml round bottom flask. Bromobenzene (157.01 mg, 1.0 mmol) was added to this mixture under stirring, followed by the as-prepared Pd NPs (5 mol%, 5.32 mg). The mixture was stirred at 100°C in an oil bath for 5 mins and then extracted with ethyl acetate (3 × 20 ml). The combined organic extract was dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and the resulting mixture was analyzed by gas chromatography (GC). In order to identify the product obtained from the catalytic reaction, the as-obtained mixture was crystallized from ethanol. The resulting white powder was identified as biphenyl using <sup>1</sup>H and <sup>13</sup>C solution

NMR and mass spectroscopy. <sup>1</sup>H NMR δ 8.25 (d, J = 8.3 Hz, 4H, C-CH, next to ipso), 7.25– 7.26 (m, 6H, remaining protons of phenyl ring); <sup>13</sup>C NMR δ 141.3 (2C, C-C, ipso), 128.8 (4C, CH-CH), 127.3 (2C, CH-CH, edge carbons), 127.2 (4C, C-CH, next to ipso); EIMS m/z 154 (M<sup>+</sup>) [32].

Soybean (*Glycine max*) leaf extract based green synthesis of palladium nanoparticles.

a) Preparation of leaf extract and synthesis of palladium nanoparticles

20g of soybean leaves were thoroughly washed with de-ionized water and cut in to small pieces. They were then boiled in 100ml of de-ionized water in a conical flask for 3 mins. Obtained soybean leaf extract was filtered and stored in a refrigerator. In order to synthesize palladium nanoparticles, 10ml of filtered soybean leaf extract was added to 200ml of ( $0.1 \times 10^{-3}$  M) palladium ion aqueous solution. The bioreduction of palladium ions and their nucleation into nanoparticles was monitored by the UV-visible spectral analysis [33].

Biological synthesis of palladium nanoparticles using leaf extract of *Sebastiania chamaelea* (L.) Muell. Arg.

a) Preparation of leaf extract and synthesis of Palladium nanoparticles

The collected leaf samples were thoroughly washed with tap water followed by distilled water to remove the surface contaminants and dried for 48 hrs under shade. The dried leaves were ground to make fine powder using mortar and pestle and sieved using a 20 mesh sieve to get uniform size range. For the preparation of the leaf broth, the sieved leaf powder of *Sebastiania chamaelea* (10g) was added to 100ml of distilled water and boiled at 70°C for 10 mins. The freshly prepared leaf broth (10ml) was re-suspended in 90ml of aqueous solution of palladium chloride and this mixture was used as a reaction medium. This reaction medium was kept at room temperature for 24 hrs. From these reaction media a small aliquot of the samples was collected separately to characterize the palladium nanoparticles that were synthesized during the above reaction. The characterization was performed through the following analyses: UV-Visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and energy dispersive X- ray analysis (EDX) [34].

Biosynthesis of palladium nanoparticles by using *Moringa oleifera* flower extract and their catalytic and biological properties

a) Preparation of extract and synthesis of palladium nanoparticles (PdNPs)

The *Moringa oleifera* flower was collected from the Durban agricultural farm and identified at the Natal Herbarium. All reagents were obtained

from Sigma-Aldrich and used without further purification. The synthesis can be summarized as follows: The flowers were dried for a few days in a dark room. The flower solution was prepared by weighing 10g of fine flower powder in a 250ml Erlenmeyer flask along with 100ml of double-distilled water and then boiling the phyto mixture for 20 mins, cooled and stored at room temperature; this concoction was used within a week. Water extracts of *Moringa oleifera* were added into conical flasks containing 1 mM palladium acetate solution. The formation of palladium nanoparticles was monitored by the improvement of light yellow color which is a characteristic of PdNPs. Different characterization carried out by UV–vis absorption spectroscopy, Zeta potential and particle size distribution, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and TGA/DSC [35].

#### Green synthesis of palladium nanoparticles using *Chlorella vulgaris*

##### a) Preparation of *Chlorella vulgaris* extract (CE)

The wet biomass of *Chlorella vulgaris* was obtained by centrifugation at 4000 rpm for 10 mins using a high-speed centrifuge. Later, the resultants were kept in incubator at 45°C for 12 hrs, until constant weight was obtained. After drying, the sample was powdered in a mortar and then approximately 0.5g of dry alga material was homogenized in 50ml double-distilled water and boiled in a sand bath for 15 mins. Finally, the crude extract was filtered through Whatman No.1 filter paper by vacuum filtration.

##### b) Synthesis of Pd nanoparticles

An aqueous solution (1 mM) of palladium chloride (PdCl<sub>2</sub>) was prepared and used for the synthesis of palladium nanoparticles. Then, about 50ml aqueous solution of 1 mM palladium chloride (PdCl<sub>2</sub>) was mixed with 10ml of crude extract of marine alga in a 150ml Erlenmeyer flask. The whole mixture was put on a magnetic heater stirrer at about 60°C and maintained in the dark. The bioreduction time of PdCl<sub>2</sub> was recorded. Different characterization carried out by UV–vis absorption spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) [36].

## Banana peel extract mediated novel route for the synthesis of palladium nanoparticles

### a) Banana peel extract (BPE) powder preparation

Peels of banana species (*Musa paradisiaca*) were washed and boiled in distilled water for 30 mins at 90°C. The peels (100g) were crushed in 100ml of distilled water and the extract was filtered through cheesecloth. This filtrate was treated with acetone and the resultant precipitate was centrifuged at 1000 rpm for 5 mins, air-dried and used for further experiments.

### b) Synthesis and characterization of palladium nanoparticles

The source of palladium is palladium chloride (PdCl<sub>2</sub>) in distilled water. Typical reaction mixtures contained 10mg of BPE powder in 2ml of palladium chloride solution (1 mM) unless otherwise stated. Other conditions included incubation at 80°C for 3 mins. The effect of pH on nanoparticle synthesis was studied by adjusting the pH of the reaction mixtures (10mg BPE, 1.0 mM palladium chloride) to 2.0, 3.0, 4.0 or 5.0. The effect of the palladium was determined by varying the PdCl<sub>2</sub> concentration (0.125, 0.25, 0.5 or 1.0 mM). The BPE powder concentration was varied (10.0, 4.0, 2.0, 1.0 or 0.5mg) while keeping the palladium chloride concentration at a level of 1.0 mM. To study the effect of temperature on nanoparticle synthesis, reaction mixtures containing 10mg BPE, and 1.0 mM PdCl<sub>2</sub> at pH 3.0 were incubated at 40, 60, 80 or 100°C. All experiments were carried out in triplicate and representative data is presented here. Synthesized palladium nanoparticles were synthesized by UV-Visible spectra, XRD analysis, SEM and EDS, dynamic light scattering and particle size analyzer and FTIR analysis [37].

## Green palladium and palladium oxide nanoparticles synthesized via *Aspalathus linearis* natural extract

### a) Biosynthesis phase

0.03g of washed and dried *Aspalathus linearis* leaves were added to 300ml of de-ionized water at room temperature for 30 mins, yielding a deep orange colored extract of pH~5. The extract was then filtered 3 times to obtain an aqueous leaf extract without any residual solid.

One has to mention that the used *Aspalathus linearis* leaves' extract is slightly fermented so as to minimize and even preclude the oxidation of



the green leaves' polyphenols. The chemical composition is very similar to that of fresh leaves.

Palladium II chloride (99.999% (Aldrich) with molecular weight of 177.33g/mol, was used as initial precursor for the biosynthesis of Pd nanoparticles. In a typical experience, 3.0g of PdCl<sub>2</sub> was added to the previous prepared *Aspalathus linearis* natural extract. At room temperature, under stirring, the Pd salt was observed to dissolve completely in the aqueous extract. The resulting solution was allowed to react over a period of 30 mins to ensure a complete oxido-reduction process of the precursor. A change in color was observed initially indicating the likely formation of Pd nanoparticles. The solution was dried in atmospheric conditions at 90°C for 1 hr to remove water and biocompounds in excess. An annealing of the biosynthesized dried sample is necessary to induce an effective crystallization. The Pd based dried sample was submitted to an annealing for 2 hrs in air at 100 and 200°C. An increase in the annealing temperature will be carried out in order to obtain a pure single phase PdO nanoparticles. Various characterizations were carried out to investigate the physical and chemical properties of the biosynthesized Pd as well as PdO nanoparticles [38].

Synthesis and characterization of palladium nanoparticles using *Catharanthus roseus* leaf extract and its application in the photo-catalytic degradation

a) Preparation of the extract

The collected fresh *C. roseus* leaves were cleaned, washed thoroughly with double-distilled water, further shade dried and pulverized into fine particles using a mechanical grinder. The pulverized plant material was extracted with petroleum ether to remove hydrocarbons followed by extraction with methanol through the soxhlet process. The collected fraction was further condensed with a rotary vacuum evaporator. About 10mg of methanolic residue was dissolved with 20ml of Milli.Q water. The plant material residue was blended uniformly with Milli.Q water.

b) Synthesis of palladium nanoparticles

About 100ml of 1 mM Pd(OAc)<sub>2</sub> solution was prepared using milli.Q water. 20ml of methanolic extract was mixed with 80ml of [Pd(OAc)<sub>2</sub>] solution and kept for continuous stirring at 60°C. The process was monitored by UV-vis spectrometry at 1 hr intervals. The plant mediated bioreduction of [Pd(OAc)<sub>2</sub>] suspended solution was monitored by UV-vis

spectrometer (Schimadzu UV–spectrophotometer, model UV-1800). Further characterization was done using Fourier transform infrared spectroscopy (FT-IR) with KBr pellets, XRD analysis (Advance Powder X-ray diffractometer, Bruker, Germany, model D8) and TEM analysis (transmission electron microscopy–Hitachi H-7100 using an accelerating voltage of 120kV and using methanol as a solvent) [39].

Green synthesis of palladium nanoparticles mediated by black tea leaves (*Camellia sinensis*) extract: Catalytic activity in the reduction of 4-nitrophenol and Suzuki-Miyaura coupling reaction under ligand-free conditions

a) Green synthesis of palladium nanoparticles using black tea leaves (*Camellia sinensis*)

Lahijan black tea leaves (*Camellia sinensis*) were supplied from the Lahijan Tea Research Center, Lahijan, Iran. 10g of the black tea was added to 100ml of de-ionized water and was boiled for 5 mins in a water bath. The mixture was then cooled down and was filtered through Whatman No. 1 filter paper to obtain aqueous extract. The filtered extract was stored in refrigerator at 4°C for further use. The extract was used as a reducing as well as stabilizing agent. For preparation of Pd NPs, 10ml of the prepared plant extract was added drop wise to 100ml of 1 mM aqueous PdCl<sub>2</sub> solution and refluxed at 100°C for 1 hr. The color of the reaction mixture gradually turned over 60 mins and indicated the formation of Pd NPs, to which acetone was added to precipitate the catalyst (Pd@B.tea NPs). After the addition of acetone (anti-solvent) the precipitated catalyst was then centrifuged at 1000 rpm for 10 mins followed by re-suspension of the pellet in Milli-Q water. The Pd loading of the prepared catalyst was measured to be 1.7 mmol/g by ICP and EDX [40].

Palladium nanoparticles: Single-step plant-mediated green chemical procedure using Piper betle leaves broth and their anti-fungal studies

a) Preparation of leaf extract and synthesis of palladium nanoparticles

The fresh P. Betle leaf extract used for the reduction of palladium ions was prepared by taking 20g of thoroughly washed, finely cut leaves in a 250ml Erlenmeyer flask along with 100ml of Millipore water and then boiling the mixture for 2 mins before decanting it. Further, the extract was filtered through Whatman No. 1 filter paper and stored for further experiments. The process of the reaction between leaf extract and aqueous palladium chloride solution was analyzed by UV-Vis absorption spectroscopy [41].

Green synthesis of palladium nanoparticles using *Hippophae rhamnoides* Linn leaf extract and their catalytic activity for the Suzuki–Miyaura coupling in water

a) Preparation of extract of the leaves of *Hippophae rhamnoides* Linn

Leaves of the *Hippophae rhamnoides* Linn were collected in June 2013 in the Sarshive region of Kurdistan province in Iran. 100g of the dried leaf powder of sea buckthorn was put into a 1000ml conical flask containing 500ml of hydroalcoholic solution (30% methanol), well mixed and then boiled for 30 mins. The extract obtained was centrifuged in 6500 rpm then filtered through a filter paper and the filtrate was kept in the refrigerator to use in the future. Furthermore, HPLC analysis was used to confirm the presence of antioxidant flavonoids inside the leaves of the plant.

b) Green synthesis of palladium nanoparticles using *Hippophae rhamnoides* Linn leaves extract

In a typical synthesis of Pd NPs, a 10ml extract of the plant leaves was added dropwise to 50ml of 0.003 M aqueous solution of PdCl<sub>2</sub> with constant stirring at 80°C. Reduction of palladium ions (Pd<sup>II</sup>) to palladium (Pd<sup>0</sup>) was completed in approx. 25 mins using monitoring by UV–vis and FT-IR spectra of the solution. The color of the reaction mixtures gradually changed from transparent yellow to dark brown in 25 mins at 80°C, indicating the formation of palladium nanoparticles; then the colored solution of palladium nanoparticles was centrifuged at 7000 rpm for 30 mins until completely dispersing [42].

Green synthesis, characterization and antibacterial efficacy of palladium nanoparticles synthesized using *Filicium decipiens* leaf extract

a) Preparation of leaf extract

Fresh leaves of *Filicium decipiens* were collected from GCT Campus, Coimbatore and its taxonomy identification was done at the Institute of Forest Genetics and Tree Breeding, Coimbatore, Tamilnadu, India. The surface of the leaves was completely cleaned with tap water and dried for ten days to remove the moisture. The dried leaves were ground to a fine powder using a kitchen blender. 5g of leaf powder was mixed with 50ml of double-distilled water and then kept in a water bath for 10 mins to obtain the leaf extract. The extract was filtered by using Whatman filter paper and stored for further use.

### b) Green synthesis of PdNPs

Green synthesis of PdNPs was carried out as follows: 10ml of aqueous F. Decipiens extract was mixed with 90ml of 1 mM PdCl<sub>2</sub> solution and kept at room temperature for 4 days. The formation of PdNPs was monitored by recording the readings using a UVspectrophotometer (Analytikjena, Germany) at the wavelength range of 400 – 900 nm. Then it was centrifuged and dried to obtain the PdNPs. Characterization studied by TEM, EDS, XRD, FTIR and UV-visible [43].

RSM optimized Moringa oleifera peel extract for the green synthesis of M. oleifera capped palladium nanoparticles with antibacterial and hemolytic properties

### a) Microwave assisted extraction process

Above 1g of M oleifera peel powder sample in methanol was placed in a microwave (Uwave 1000, 220 V/50 Hz, Sineo microwave, UV, US synthesis extraction reactor, China). Different variables, such as microwave power (300, 400 and 500W), temperature (60, 65 and 70°C) extraction time (1, 2 and 3 mins), solvent quantity (20, 25 and 30ml/g) of methanol portion (100%) were applied in order to obtain a good yield of extract.

### b) The RSM design for the extraction of M. oleifera extract

To discover the appropriate extraction conditions for the M. Oleifera peel extract, RSM methodology was used. Symmetrically, there are four levels that were used with the 29-run BBD quadratic model. This was utilized to optimize the effectiveness of each variable, such as microwave power (W, A), temperature (°C, B), irradiation time (mins, C) and solvent to solid ratio (ml, D).

The quadratic polynomial equation was used to find a suitable variable as described below.

$$Y = \beta_0 + \beta_1(A) + \beta_2(B) + \beta_3(C) + \beta_4(D) + \beta_{11}(A^2) + \beta_{22}(B^2) + \beta_{33}(C^2) + \beta_{44}(D^2) + \beta_{12}(AB) + \beta_{13}(AC) + \beta_{14}(AD) + \beta_{23}(BC) + \beta_{24}(BD) + \beta_{34}(CD)$$

Where,  $\beta_0$  is the constant co-efficient of the model, ( $\beta_1, \beta_2, \beta_3, \beta_4$ ), ( $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ ) and ( $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}$  and  $\beta_{34}$ ) are regression

coefficients, A (watts), B (temp), C (mins) and D (solvent ratio) are coded variables.

c) Synthesis of Pd NPs using *M. oleifera* peel extract

A microwave irradiation method was followed for the synthesis of PdNPs, in this process Pd(OAc)<sub>2</sub> (1mM, 80ml) solution was mixed with the 20m of RSM optimized methanolic extract of *M. oleifera* peel. The reaction mixture was placed in the microwave cabin and subjected to irradiation at 300W for 5 mins. The centrifugation was carried out to remove the nanoparticles from the reaction mixture using 4000 rpm (15 mins). The calcination procedure was employed at 300°C. The *M.oleifera* capped Pd NPs was stored in a refrigerator for further use [44].

*Sapium sebiferum* leaf extract mediated synthesis of palladium nanoparticles and *in vitro* investigation of their bacterial and photocatalytic activities

a) Extraction of phytoconstituents from *Sapium sebiferum* leaves

*Sapium sebiferum* leaves were collected from Lakki Marwat, Pakistan and thoroughly washed with de-ionized water to remove any dust particles. A grinder was then used to convert these plant leaves into powder. 10g of the plant powder was then heated at 70°C for 2 hrs in 100ml of distilled water. The Whatman No. 3 filter paper was used for the filtration of the leaf extract. After that, the extract was centrifuged (1000 rpm) at 4°C to remove the residual solid impurities.

b) Synthesis of Pd nanoparticles using *Sapium sebiferum* leaf extract

Pd nanoparticles were synthesized by mixing 0.003 mM palladium chloride (PdCl<sub>2</sub>) in 50ml of water and 10ml of *Sapium sebiferum* leaf extract in a 100ml beaker. It was magnetically stirred in dark conditions until the color changes occurred from light brown to dark brown. After the formation of Pd nanoparticles, it was dried in a 6ES freeze drier [45].

### 3. Platinum

Biological synthesis of platinum nanoparticles using Diopyros kaki leaf extract

a) Preparation of leaf broth

Persimmon (*D. kaki*) leaves were collected and left to dry for 2 days at room temperature. Leaf broth solution was prepared by boiling a mixture of 5g of thoroughly washed and finely cut dried leaves and 100ml of sterile distilled water in a 300ml Erlenmeyer flask for 5 mins. The solution was decanted and stored at 4<sup>0</sup>C; it was used within a week of being prepared.

b) Synthesis of palladium nanoparticles

Our general method for reducing PtCl<sub>6</sub><sup>2-</sup> ions was to add 10ml of leaf broth to 190ml of 1 mM aqueous H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. The reaction was performed with reflux at various temperatures, between 25°C and 95°C, in order to investigate the effects of temperature on platinum nanoparticle synthesis rate and size. The concentrations of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O solution and leaf broth were also varied, between 0.1–2 mM and 5–50% by volume, respectively. The resulting platinum nanoparticle solution was purified by repeated centrifugation at 15,000 rpm for 20 mins, with the pellet produced by this process redispersed in de-ionized water. Ultraviolet– visible (UV–Vis) spectra were recorded as a function of the reaction time on a UV-1650CP Shimadzu spectrophotometer operating with a resolution of 1 nm. Purified platinum nanoparticles were freeze-dried, and their structure and composition analyzed by high-resolution TEM (HR-TEM; JEOL-2010), energy-dispersive X-ray spectroscopy (EDS; Sigma), X-ray photoelectronspectroscopy (XPS; ESCALAB 210), and FTIR (BomemMB100). Platinum concentrations and conversions were determined with inductively coupled plasma spectrometry (ICP; JY38Plus), and the average particle size ascertained from TEM micrographs [46].

## Biological synthesis of platinum nanoparticles: effect of initial metal concentration

### a) Preparation of cell-free soluble extract (CSE)

The SRB cells were cultured under anaerobic conditions and harvested as previously described [70]. The cell pellet was washed thoroughly in ddH<sub>2</sub>O to remove any sulfide or sulfate which could result in the precipitation of the platinum salt in the solution as a metal sulfide. The cells were resuspended in minimal volume ddH<sub>2</sub>O (50ml) containing sodium cholate (2%) to solubilize the membrane proteins and sonicated using a Vibracell sonicator (Sonics and Materials Inc., USA) at 10W for 4 mins (30 sec intervals) at 4°C. The homogenate was then centrifuged (18,000×g, 20 mins, 4°C) and the resulting supernatant was dialysed overnight at 4°C against ddH<sub>2</sub>O using Snakeskin® Pleated Dialysis tubing (MWCO 10 kDa) to remove the salts, any residual sulfates/sulfides and small molecular weight proteins. To minimize bacterial growth the CSE was maintained at 4°C and 100gml<sup>-1</sup> ampicillin and 25gml<sup>-1</sup> tetracycline-hydrochloride added.

### b) Preparation of cell-free soluble extract (CSE)

Prior to experimental set-up and pH adjustment, the CSE crude solution was incubated on ice for 10 mins to minimize any enzymatic activity. A total volume of 5ml, consisted of 250gml<sup>-1</sup> protein from the CSE and H<sub>2</sub>PtCl<sub>6</sub> [representing the Pt(IV) ion] ratios to protein ranging from 0.7:1 to 4:1. The pH was adjusted to 9.0 with 1M NaOH and the final volume was made up with ddH<sub>2</sub>O. ‘0 h’ was taken as the point after pH adjustment while still on ice. After pH adjustment the samples were placed in an incubator at 65°C in the dark, where triplicate samples (300l) were taken at regular intervals (0, 0.5, 1, 2, 4, 6, and 8 hrs). Controls were set-up as above with the exception of the CSE volume being replaced by ddH<sub>2</sub>O. All samples were analysed by UV-vis spectroscopy with a PowerWave (Bio-Tek, Instrumental Inc., USA), at 261 and 334nm for Pt(IV) and Pt(0) respectively and platinum ion concentrations were calculated from a standard curve. Pt(0) concentration could not be assayed directly due to the inherent problems associated with nanoscale platinum materials resulting in a lack of an appropriate standard curve. Hence, an absorbance of 334nm was selected as an “indicator” of nanoparticle formation over time [47].

## Rapid biosynthesis of platinum and palladium metal nanoparticles using root extract of

### *Asparagus racemosus* Linn

#### a) Preparation of extract

The synthesis of platinum and palladium nanoparticles has been carried out using the root extract of *Asparagus racemosus* Linn. The tubers of *Asparagus racemosus* were collected from the nursery of the Mahim Nature Park, Mumbai. The healthy and matured tubers were selected and washed thoroughly. The epidermis was peeled off with the help of a scalpel and the pith was separated with the help of forceps to get the cortex. 5g of the cortex was homogenized in a mortar and pestle and suspended in 100ml of de-ionized water. The suspended mass was then filtered out; the filtrate obtained contained the bioactive components leached from the tubers. This filtrate was used as the extract for the preparation of platinum and palladium nanoparticles. Metal salts platinum (IV) chloride, 99.9% and palladium (II) chloride 59% Pd were purchased from Hi Media India Ltd. and Fisher Scientific, respectively, and were used as received.

#### b) Synthesis of platinum and palladium nanoparticles

In the separate experiments conducted with the 10ml of tuber extract, 0.1ml of 100 mM metal salt (Platinum tetrachloride / Palladium (II) chloride) solution was mixed rapidly. Similarly, two control samples in one plant extract and in another solution of metal ion were also maintained. The reaction mixtures along with controls were exposed to the sunlight for 5 mins under static conditions [48].

### Plant-mediated synthesis of platinum nanoparticles and its bioreductive mechanism a) Preparation of extract

The biomass of *Cacumen Platycladi* for reduction was milled, and the powder was screened with a 20-mesh sieve. 3g of the powder was then dispersed in 90ml of de-ionized water in a 200ml beaker and boiled for 5 mins. Thereafter, the resulting broth was cooled to room temperature and filtered to obtain the filtrate, which was subsequently adjusted to 100ml by adding de-ionized water. The resulting CPE was refrigerated at 6°C for the biosynthesis of PtNPs within 7 days after preparation.



### b) Synthesis of PtNPs

In a typical synthesis for the PtNPs, 10ml of CPE was first heated at constant temperatures of (30, 60, and 90°C) in an oil bath, stirring for 10 mins. Afterward, an amount of aqueous  $\text{Na}_2\text{PtCl}_4$  (52.24 mM) was added suddenly to the flask in order that the reaction solution possessed the initial  $\text{Na}_2\text{PtCl}_4$  concentrations of 0.5, 1, 1.5, or 2 mM [49].

Plant-mediated synthesis of platinum nanoparticles using water hyacinth as an efficient biomatrix source: an eco-friendly development

#### a) Preparation of plant extract and biosynthesis of colloidal Pt-NPs

10g of finely cut fresh leaves of WH plant was extracted with 200ml of distilled water at 60°C for 10 mins and filtered. The filtrates were stored at 4°C for further use. In a typical synthesis, 5ml of the WH extract was added to 50ml of an aqueous solution of hexachloroplatinic acid ( $1 \times 10^{-3}$  M) in a sealed 3-necked flask and maintained at 90°C for 1 hr. The same reaction was repeated in the absence of leaf extract. Biosynthesized Pt-NPs was monitored visually by using a UV/Vis spectrophotometer in the range 200 -700 nm. TEM analysis was done using FEI Tecnai 20 equipped with a LaB6 emitter, operating at 200kV. FTIR analysis of WH extract and biogenicPt-NPs were carried out using a Spectrum Two Perkin Elmer. The DLS analysis was carried out using a Malvern zeta sizer Nano series [50].

Biofabrication of platinum nanoparticles using *Fumariae herba* extract and their catalytic properties

#### a) Preparation and synthesis of platinum nanoparticles

4g of dried and powdered herbs were put into 180ml of double-distilled water. The mix was kept at 90°C for 45 mins with vigorous magnetic stirring. Fresh extract was used immediately in all studies after filtration through Whatman's No. 1 filter paper. Then, 10ml of the prepared extract was collected and there was added 0.004g of  $\text{K}_2\text{PtCl}_6$ . The solution was mixed under magnetic stirring for 4 hrs at a temperature of 50°C. The color changed from yellow to brown, which indicated the formation of platinum nanoparticles [51].

## Green synthesis and the characterization of platinum nanoparticles using quail egg yolk

### a) Synthesis of Pt nanoparticles

This study was begun just after the quail eggs were obtained. In order to prepare the green synthesis reaction medium, the white and yolk of the quail eggs were separated from each other. 1ml of egg yolk was added to 99ml of distilled water and mixed by using a magnetic stirrer for 30 mins to prepare a homogeneous reaction medium. Then the homogenate was allowed to leach out heterogeneous components through filtration. The obtained egg yolk homogenate was used as the reaction medium for the green synthesis. Firstly, 2ml of 10.0 mM  $\text{H}_2\text{PtCl}_6$  solution was added to the mixture to prepare the reaction medium (100ml) quickly. The green synthesis reaction medium was stirred by using a magnetic stirrer at normal atmospheric pressure at 100 rpm and kept at room conditions. Formation of the reaction was monitored with the help of a spectrophotometer for 72 hrs. For this purpose, platinum chloride transforming to the metallic nano platinum was scanned using the spectrometer between 200 and 1000 nm. In this way, the wavelength giving maximum absorbance of nano platinum was detected. Later, this wavelength was used to determine the optimization process [52].

## Green synthesis of platinum nanoparticles using *Azadirachta indica*: an eco-friendly approach

### a) Collection and extract preparation

The plant (*A. indica*) leaves were collected from our campus, and allowed to dry for 2–3 days at room temperature. The plant leaf broth solution was prepared by taking 5g of thoroughly washed and finely cut leaves placed in a 250ml Erlenmeyer flask with 100ml of sterile deionised water and then boiled for 5 mins. The solution was stored at 4°C and used within a week.

### b) Synthesis of platinum nanoparticles

The general method was adopted for the synthesis of platinum nanoparticles. 10ml of neem leaf broth was added to 190ml of 1 mM aqueous  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ . The mixture was maintained at 100°C in a sealed flask to avoid evaporation for 1 hr on the hot plate, since the temperature catalyses the rate of reduction process. For a control experiment, the same amount of platinum solution was maintained separately under the same

reaction conditions. The reduced platinum solution was sonicated for 30 mins so as to disperse the nanoparticles in liquid in order to break the particle agglomerates. The reduced platinum metals were purified by repeated centrifugation at 15,000 rpm for 20 mins, and the pellets were washed with distilled water to remove the impurities. The purified platinum nanoparticles were subjected to characterization studies [53].

Prunus x yedoensis tree gum mediated synthesis of platinum nanoparticles with antifungal activity against phytopathogens

a) Gum extract preparation, synthesis, and optimization of PtNP production

Tree gum of *P. yedoensis* (50g) was collected in and around Chonbuk National University, Iksan, South Korea during June, 2015 (Fig. 1) and then washed thoroughly with copious amounts of nanopure water. Briefly, the PYTG was dried at 70°C for 5 hrs, powdered using a mortar and pestle, and sieved to obtain a mean particle size. Then, 0.5% (w/v) of homogenous PYTG stock was prepared by autoclaving for 20 mins at 121°C, corresponding to a steam pressure of 103 kPa (15psi). The obtained solution was used for further experiments. Typical reaction mixtures contained 20ml of PYTG autoclaved solution with 100ml of 0.1 M chloroplatinic acid. During the reaction, a brown-colored reaction mixture was the initial visual confirmation of PtNPs. Obtained nanomaterial was freeze-dried at -80°C and used for characterization and antifungal studies. PtNP production optimization considered various parameters, such as pH (2, 3, 4, 5, 6, 7, 8, 9, and 10), gum extract (1, 2, 3, 4, 5, 6, 7, 8, and 9%), metal ions (0.25, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mmol), and time (5, 15, 30, 45, and 60 mins). While optimizing pH, other parameters such as gum extract (5%), metal ions (1.0 mmol), and time (30 mins) remained stable [54].

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# CHAPTER FOUR

## APPLICATIONS

### Materials

**As Insulation materials:-** Nanocrystalline materials synthesized by the sol-gel technique exhibit a foam-like structure called an “aerogel” [1]. Aerogels possess low thermal conductivity, are extremely lightweight, porous, and 3-D, containing continuous networks of particles and voids.

**As Nanocomposites:-** These are the materials that combine more than two components, and are designed in such a way that they exhibit properties such as: biological, optical, electrical, magnetic, mechanical, physical, etc. of each component. Nanocomposites containing CNT and polymers used to control their conductivity are interesting for a wide range of applications, such as supercapacitors, sensors, solarcells, etc. [2].

**Paints:-** Nanoparticles confer enhanced desired mechanical properties on composites such as Biointerphases vol. 2, issue 4 (2007) pages MR17 - MR172 86scratch resistant paints based on encapsulated nanoparticles [3].

### Mechanical engineering

**Cutting tools:-** Tools made of nanocrystalline materials (such as tungsten carbide, WC) are much harder than their conventional equivalents due to the fact that the microhardness of nanosized composites is increased compared to that of microsized composites [4].

**Lubricants:-** Nanospheres of inorganic materials could be used as lubricants, acting as nanosized ball bearings [5].

### Biomedical applications

**Nanoscaffolds:-** Nanofiber scaffolds can be used to regenerate central nervous system cells and possibly other organs. Experiments performed on a hamster with a severed optic tract demonstrated the regeneration of axonal tissue initiated by a peptide nanofibers scaffold [6].

**Antimicrobial nanopowders and coatings:-** Certain nanopowders possess antimicrobial properties [7]. When these powders contact cells of *E. coli*, or other bacteria species and viruses, over 90% are killed within a few minutes. Due to their antimicrobial effect, nanoparticles of silver and titanium dioxide (<100nm) are assessed as coatings for surgical masks [8].

**Bio-separation:-** Nanotube membranes can act as channels for the highly selective transport of molecules and ions between solutions that are present on both side of the membrane [9]. For example, membranes containing nanotubes with inside diameters of molecular dimensions (less than 1 nm) separate small molecules on the basis of molecular size, while nanotubes with larger inside diameters (20–60 nm) can be used to separate proteins [10].

**Drug delivery:-** The ability of nanoparticles to target and penetrate specific organs and cells contributes to their toxicity, something that may be exploited in nanomedicine. Nanospheres composed of biodegradable polymers can be incorporated in drugs, allowing the timed release of the drug as the polymer degrades [11]. When particles are set to degrade in an acid microenvironment, such as tumor cells or around inflammation sites, this allows site-specific or targeted drug delivery.

**Gene transfection:-** Surface-functionalized nanoparticles can be used to permeate cell membranes at a much higher level than nanoparticles without a functionalized surface [12]. This property can be used to deliver genetic material into living cells, a process called transfection. For example, silica nanospheres labelled on their outer surfaces with cationic ammonium groups can bind DNA (a polyanion) through electrostatic interactions [13]. Then nanoparticles deliver the DNA into cells.

**Medical imaging:-** A variety of techniques currently called “non-invasive” have been used for more than a quarter of a century in medical imaging, for example, superparamagnetic magnetite particles coated with dextran are used as image-enhancement agents in magnetic resonance imaging [14]. Intracellular imaging is also possible through the attachment of quantum dots to selected molecules, which allows intracellular processes to be observed directly.

**Nasal vaccination:-** Nanosphere carriers for vaccines are in development. Antigen-coated polystyrene nanospheres, used as vaccine carriers targeting human dendritic cells, have been researched for nasal vaccination. Nanospheres have a direct effect on human dendritic cells, inducing

transcription of genes important for, e.g., phagocytosis as well as an immune response.

**Nucleic acid sequence and protein detection:-** Targeting and identifying various diseases could be made possible by detecting nucleic acid sequences unique to specific bacteria and viruses, or to specific diseases or abnormal concentration of certain proteins that signal the presence of various cancers and diseases [15]. Nanomaterial-based assays are currently evaluated as well as more sensitive protein detection methods. Nucleic acid sequences are currently detected with polymerase chain reaction (PCR) coupled with molecular fluorophore assays. Despite high sensitivity, PCR has significant drawbacks, such as: complexity, sensitivity to contamination, cost, and lack of portability [15]. Current protein detection methods, such as enzyme-linked immunoabsorbent assay (ELISA), only allow the detection of protein concentrations at a time when the disease is often advanced. More sensitive methods based on nanomaterials would revolutionize the physical treatment of many cancer types and diseases [15].

**Smart nanophase extractors:-** Differentially functionalized nanotubes are used as smart nanophase extractors with molecular-recognition capabilities to remove specific molecules from solutions [10].

**Treatment for local anesthetic toxicity:-** Local anesthetic can sometimes be very toxic, ranging from local neurotoxicity to cardiovascular collapse and coma. In addition to conventional therapies, drug-scavenging nanoparticles have shown to increase survival rate from no animals in the control group to all animals in the treated group [16], [17].

### a) Gold

Gold has a broad range of applications because it possesses interesting properties and accordingly it is used widely. Below, several applications of biogenic gold nanoparticles from plants are itemized [**Table 4.1**].

No.	Plant used for the synthesis	Uses	References
1.	<i>Gymnocladus assamicus</i>	Catalytic activity in reduction of 4-nitrophenol to 4-aminophenol	18
2.	<i>Sesbania grandiflora</i>	Catalytic activity on reductions of methylene blue	19
3.	<i>Eucommia ulmoides</i>	Decoloration of Yellow 179 and Congo red	20
4.	<i>Nerium oleander</i>	Antioxidant study	21
5.	<i>Suaeda monoica</i>	Antioxidant activity	22
6.	<i>Psidium guajava</i>	Protein Tyrosine Phosphatase 1B inhibitory activity	23
7.	<i>Punica granatum</i>	<i>In vitro</i> cytotoxicity (MCF-7)	24
8.	<i>Solanum nigrum</i>	Antibacterial and free radical scavenging activity	25
9.	<i>Hibiscus cannabinus</i>	Antibacterial activity	26
10.	<i>Euphorbia hirta</i>	Antibacterial activity	27
11.	<i>Abelmoschus Esculentus</i>	Antifungal activity	28
12.	<i>Barbated skullcup</i>	Can raise electronic transition between the electrode and the <i>p</i> -nitrophenol	29
13.	<i>Acalypha indica</i> Linn	Human breast cancer	30
14.	<i>Blue green alga</i>	Antibacterial	31
15.	<i>Achyranthes aspera</i> Linn	Anticancer	32
16.	<i>Terminalia arjuna</i>	To enhance seed germination activity of <i>Gloriosa superba</i>	33
17.	<i>Padina pavonica</i>	Antibacterial activity against human pathogens	34

**Table 4.1 – Plants used in biogenic gold synthesis and its applications**

**Therapeutic Agent Delivery:-** Therapeutic agents can be coated on the surface of the gold nanoparticles. Due to their large surface area to volume ratio, gold nanoparticles allow their surface to be coated with hundreds of molecules, such as therapeutics, biomolecules, targeting agents, etc.

**Diagnostics**– In the diagnosis of heart diseases, cancers and infectious agents, gold nanoparticles are used to detect biomarkers. Also common in the lateral flow of immune assays: a familiar example being the home pregnancy test.

**Catalysis**– Gold nanoparticles play an important role as a catalyst in a number of chemical reactions. For selective oxidation the surface of the gold nanoparticles is used and, in some cases, the surface can effect a reduction in the reaction (nitrogen oxide). Gold nanoparticles are being developed for fuel cell applications, and these technologies would be useful in the automotive field and display industry. In cancer therapy gold nanoparticles act as photothermal agents, drug carriers, contrast agents and radiosensitizers.

- Gene Detection.
- Antibiotics.
- Anti-inflammatory activity.
- Given their unusual optical, electrical and mechanical properties, gold nanoparticles and gold nanowires have been widely used as building blocks for sensing devices in chemistry and biochemistry fields.
- Imaging Techniques
  - Conventional Techniques:- X-ray, MRI, Fluoroscopy, CAT scan
  - Tracking blood flow:- Tag proteins of cells with gold nanoparticles, view process of angiogenesis
- Cancer Imaging :-
  - Injection of gold nanoparticles
  - Localization around tumors
  - CT scan shows cancerous regions
- Negative biological side-effects:
  - Toxicity of quantum nanodots
  - Effects on living organisms not well known
- Gold nanoparticles safer
  - Biologically inert
  - Will not interact with other chemicals
- Antagonistic activity against Bacteria and Fungi.



### b) Palladium

Palladium exhibits a wide range of applications in catalytic reactions. Below several applications of biogenic palladium nanoparticles from plant are itemized [Table 4.2].

No.	Plant used for the synthesis	Uses	References
1	<i>Pulicaria glutinosa</i>	Catalytic activity towards the Suzuki coupling reaction	32
2	<i>Moringa oleifera</i>	Catalytic	35
3	<i>Catharanthus roseus</i>	Photo-catalytic degradation	39
4	<i>Camellia sinensis</i> (black tea)	Catalytic activity in the Reduction of 4 nitrophenol and Suzuki- Miyaura coupling reaction under ligand-free conditions	40
5	<i>Piper betle</i>	anti-fungal studies	41
6	<i>Hippophae rhamnoides</i> Lin	Catalytic activity for the Suzuki–Miyaura coupling in water	42
7	<i>Filicium decipiens</i>	Antibacterial	43
8	<i>Moringa oleifera</i>	Antibacterial and hemolytic property	44
9	<i>Sapium sebiferum</i>	Bacterial and photocatalytic activities	45

**Table 4.2 – Plants used in biogenic palladium synthesis and its applications**

- An excellent hydrogenation and dehydrogenation catalyst available in organo-metallic forms found to be effective in a number of chemical reactions due to its large surface area.
  - Antibiotics
  - Cancer therapy

### c) Platinum

Platinum nanoparticles used in catalytic reaction, antibiotics, etc. Here several applications of biogenic platinum nanoparticles from plants have been mentioned [Table 4.3].

No.	Plant used for the synthesis	Uses	References
1	<i>Cacumen Platycladi</i>	Bioreductive mechanism	49
2	<i>Fumariae herba</i>	catalytic properties	51
3	<i>Prunus x yedoensis tree gum</i>	Antifungal activity against phytopathogens	54

**Table 4.3 – Plants used in biogenic platinum synthesis and its applications**

- Exhibit high corrosion resistance.
- Antibiotic.
- Used in number of catalytic applications.
- Combination of platinum nanoparticles with irradiation effectively used in Hadron therapy (fast ion radiation) improves cancer therapy protocols.
- Cancer therapy due to its excellent anti-oxidant properties.
- Used in Magnetic nanopowders, polymer membranes, coatings, plastics, nanofibers and textiles.

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# CHAPTER FIVE

## SUMMARY

Current research on humans and animals indicates that metal nanoparticles rapidly migrate to organs through the circulatory system followed by the blood, cells and tissues in the body. That such nanoparticles have the ability to effect the biochemical functions within the organisms is imperative, because genetic factors often play an important role in the response of an organism to the metal nanoparticles. Pre-existing diseases such as asthma and diabetes, for example, may be prone to the harmful effects of metal nanoparticles. In some cases, the toxic properties of metal nanoparticles can be harnessed for the improvement of human health by targeting cancer cells, harmful bacteria and viruses. But this may also have secondary negative effects on health, for example, metal nanoparticles being used for targeted cancer therapy may cause harmful effects elsewhere in the body.

This review book describes the unique physical and chemical methods for the biogenic synthesis of gold, palladium and platinum nanoparticles. Gold, palladium and platinum nanoparticles exhibit unique physical and chemical properties. In addition, this book describes the mechanism of biological synthesis that occurs during reactions where plasmonic properties and surface chemistry plays an important role. Surface chemistry and plasmonic properties are responsible for allowing the stable interaction of biologically active compounds, and can also bind with ligands through hydrophobic interactions. These metal nanoparticles have emerged as promising carriers for biomolecules, such as proteins, nucleic acid, peptides, drug molecules, etc. Due to their multifunctionality, low inherent toxicity, high surface chemistry, electromagnetic properties, reactivity, kinetics, aggregation, photo physical and optical properties they impart unique characteristics in the fields of chemotherapy, bacterial diagnosis, cancer diagnosis, imaging and drug delivery. Thus, all of these properties open up many different uses for gold, palladium and platinum nanoparticles in biomedical applications such as gene detection, antibiotics, cancer therapy, anti-inflammatory activity, catalyst, imaging, phytochemical reactions, therapeutic diagnosis, etc.

The summaries above includes periodic written reviews and research articles that, together, encompass the collected knowledge on biologically synthesized metal nanoparticles, characterizations, properties and mechanisms, and presents them in a comprehensible format for a wide audience of researchers. Significantly, an important issue that needs to be highlighted is the engineering of the nanoparticles surface for optimizing properties such as non-immunogenicity and bioavailability for various biomedical applications. From the perspective of current research, this is a field that needs further rigorous exploration.