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Plant Extract: An Effective Medium for Synthesis of Metal Nanoparticles

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Abstract

Over the past few decades, nanoparticles of noble metals and certain metal oxides such as silver and zinc oxide respectively had exhibited significantly distinct physical, chemical and biological properties from their bulk counterparts. Nano-size particles of less than 100nm in diameter are currently attracting increasing attention for the wide range of new applications in various fields of industry. Although there are several synthesis modes, what so ever, the best mode is bio-synthesis which is dependent on the Phytomining and Biosilicification. These processes describes the ultimate reducing agent is plant itself. However, it is being continued to search that which bio molecule is responsible for the reduction of metals into nanoparticles. There are few processes in the synthesis of metal Nanoparticles which were rapid without any toxicity just by using two components as of silver. Apart from this synthesis of other important nanoparticles like gold, zinc oxide and simultaneous synthesis of gold, silver and platinum is also described. The reported plants for the synthesis of various nanoparticles and their respective sizes were also described.

Keywords: Nanoparticles, Physicochemical, Phytomining

Introduction

Nanoscience nowadays is a fast emerging field focusing on broad range of synthesis and application of different nanomaterials. This field is considered to be a conclusion for solving many stiff-necked problems in multidisciplinary fields such as pharmaceutical sciences, applied physics, material sciences, colloidal sciences, device physics, supramolecular chemistry, mechanical, and electrical engineering etc. Nanomaterials have received much attention because of their structure and properties varying from those of atoms, molecules with respect to their bulk materials and thus having many potential applications [1]. Nanoparticles are referred to those particles with size up to 100nm. Nanoparticles production can be achieved by physical, chemical and biological methods. Biological approaches would be beneficial compared the remaining two methods because of its nontoxic, development of clean, environmentally acceptable green chemistry procedures. Over the last few decades, it was only the prokaryotes like bacteria, fungi, viruses have been exploited for the capability to biosorb and bioreduce insoluble toxic metal ions to soluble non-toxic metal salts or change in valency. But recently, it was found that highly evolved organisms like plants, algae, diatoms, human cell and other components of eukaryotes also possess the reducing potential to convert the inorganic metal ions to metal nanoparticles. Phototrophic eukaryotes acquire energy from sunlight through photosynthesis and fixes inorganic carbon into organic materials, whereas heterotrophic eukaryotes like human cells use organic carbon produced by other organisms for growth. Eukaryotes in its genetic material possess information to act as reducing and stabilizing agents. Using Biotechnology techniques, Molecular cloning and genetic engineering of genes encoding specific enzymes or components that mediate the bioreduction of metals can be explored to promote the facile synthesis of nanomaterials. The first successfully report of synthesis of nanoparticles assisted by living plants appeared in 2002 from alfalfa seedlings [1]. Green synthesis protocols are more advantageous and opposed to Physicochemical processes because of its cost effectiveness for bulk production as these processes avoids the usage of high temperature, energy, pressure and mainly toxic chemicals. Further, it was also reported that the extracellular production of nanoparticles is more advantageous for large scale production [2]. Using plants for nanoparticles production is beneficial over other biological processes by eliminating the elaborate process of maintaining cell culture [3]. If biological synthesis of nanoparticles can compete with chemical methods, there is a need to achieve faster synthesis rates. The size and shape of the nanoparticle depends on the various parameters like P^H, temperature and time of reaction, nature of plant

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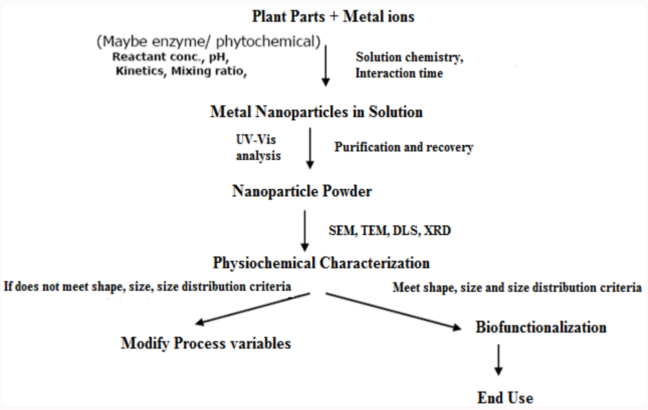

Figure 1: Flowchart representing the Biosynthesis of Nanoparticles using plants.

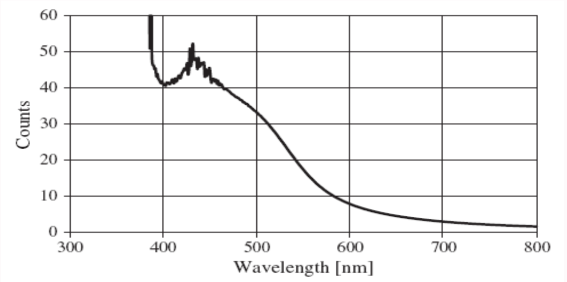

Figure 2: Depicting the UV-Vis absorption spectra with characteristic peak at 450nm indicating AgNPs formation [30].

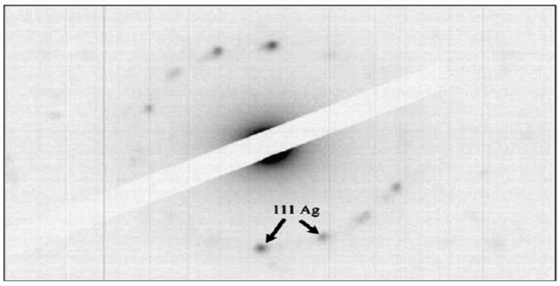

Figure 3: TEM representing SAD pattern (invert image), the discrete spots in the ring is characteristic of the single crystalline structure of each individual particle [30].

extract, the relative concentrations of the extract and metal salts reacting as well as the rate of mixing of plant extract and metal salts [4]. The stability of produced nanoparticles can in some cases change after a few days or the nanoparticles can remain stable over long periods. Mostly the nanoparticles from plants are metal nanoparticles. Otherthan the surface to volume ratio, surface energy, spatial confinement and reduced imperfections, metal nanoparticles have unusual significant optical, photoelectrochemical, electronic, chemical, mechanical, magnetic, thermal, dielectric, biological properties as opposed to the bulk. Metal nanoparticles are found to be used in optical detectors, laser, sensor, imaging, display, solar cell, photocatalysis, photochemistry, biomedicine, pharmaceutical applications, magnetic materials and information storage and so on [1]. Owing to wide range of application, an immense demand to obtain nanoparticles in non agglomerated, uniform with a well controlled mean size and narrow distribution is prerequisite for Optoelectronic, physicochemical and electronic properties which are mainly dependent on the size, shape and crystallinity. Therefore, the synthesis of monodispersed nanoparticles with different sizes and shapes has been a challenge. In the recent years, these challenges have been processed and seemed to be favored by the Plant mediated synthesis. The objective of this study mainly deals with the Principle of plant mediated Biosynthesis of nanoparticles which includes the Phytomining and rare process, Biosilcification which occurs in higher plants. The mechanism involved within the plants deals with the intracellular and extracellular mode of synthesis. Nonetheless, they are still huge number of conflicts in related to the Perfect mechanism in plants in both the modes. The rapid synthesis of several metal nanoparticles are briefly described along with its characterization and its applications.

Principle and Mechanism Involved in the Synthesis of Nanoparticles from Plants

Plants will accumulate the metals from soil by means of Phytomining. Anderson et al were the first to report the accumulation of gold in *Brassica juncea*. Phytomining involves growing hyper accumulator plants on a mineralized soil or low-grade ore body and then harvesting, incinerating the produced biomass in order to produce a commercial bio-ore [5]. In case of non-accumulator species, for suppose Gold being metal is insoluble in soil solution and therefore unavailable for uptake by some plants. The addition of chelating agents such as thiocyanate to the soil to complex and solubilize gold can overcome this problem. This strategy in the plants is known as 'induced hyper accumulation' which is usually done for huge production mediated biologically which was reported in *Brassica juncea*. Nanoparticles can be synthesized both inside the living plants and within the sun dried biomass [6,7]. Phytoremediation is ultimate key concept on which the synthesis of metallic nanoparticles is based upon [8]. Besides, in some higher plants Biosilcification is also common. Silicic acid is taken up through the plant roots and transported as a silicon complex through the xylem. When this complex reaches the stems or leaves, where mineral deposition should occur, its breakdown is triggered by change in pH, inducing the release of silicic acid that will further condense to form the silica [9,10]. Perry and Keeling Tucker reported that proteins, proteoglycans help in catalysis of silica polycondensation and in structure direction during the formation of silica structures in *Equisetum telmateia*. The basic mechanism in all cases involves the accumulation of nanoparticles after the reduction of metal ions [11]. Definitely this reduction process is mediated may be by some reducing agents, enzymes bound to the cell wall, proteins, polysaccharides, phytochemicals, amino acids and vitamins etc [12]. Park et al. recently reported that the mostly Phytochemicals like primary and secondary metabolism products such as antioxidants, flavonoids, flavones, isoflavones, catechins, anthocyanidins, isothiocyanates, carotenoids, polyphenols are responsible for the reduction [13]. It was reported that the stress tolerant plants have high influence on the synthesis of nanoparticles by reducing metal in compared to other plants [14]. Till date, many studies have been focused on the metal uptake by plants, particularly by phytoremediation and hyper accumulation and few reports have distinguished between elemental metal deposition and metal salt accumulation, quantification of the proportion of the salts converted to metal nanoparticles has only rarely been addressed [15,16]. The metabolic function of plants results in Biomineralisation or the precipitation of minerals. Metabolism creates heterogeneous accumulations, composites of organic and inorganic compounds, within homogeneous distributions that reflect the environment in which they form. Minerals produced in living organisms include carbonates, phosphates, sulfates, sulfides, hydrate silica, metals, oxides, hydroxides and organic minerals. In higher plants, mostly calcium oxalate and silica are present [17]. Although the dynamics of deposition of metal nanoparticles was still not figured out but the synthesis and storage of metal nanoparticles in the tissues of plant must have some bio-available form in the growth medium. Soon after the root uptake, the element is transported across the root membrane and trans located in different parts of the plant. Once transported into the plants, the reduced metals are deposited in nanoparticles of various shapes and sizes. Still there is a confusion, whether Nanoparticles are formed outside the plant and then transported through the root membrane into the plant [18], or whether nanoparticles are formed within the plant by the reduction of the metal salt [19]. The most reliable hypothesis is that the ionic form of the element must be transported across the root membrane, then trans located in the plant and reduced to the elemental form [20]. Recently Beattie and Haverkamp investigated tissues of *Brassica juncea* to know the mechanism of nanoparticle formation by localising gold and silver nanoparticles formation. The final outcome from several experiments reports that the site of abundant reduction of metal salts to nanoparticles is chloroplasts, in which high reducing sugars like glucose and fructose are responsible for the reduction of Au and Ag [21] (Figure 1).

Production of Silver Nanoparticles (AgNPs) using Plants

AgNPs receive enormous scientific, technological and commercial attention due to their unique size and shape dependent properties. Historically, silver compounds and ions have been extensively used for both hygienic and healing purposes [22]. These exhibit drastic variation in their physicochemical properties with the size, shape, and their conjugation with other organic/ biological substances thus gaining one of most important challenges in the field of nanotechnology. Due to its enhanced physicochemical and biological properties activities compared to the bulk materials, these have been applied as anti-infection agent due to the advent of antibiotics and as disinfectants for medical devices and also for home appliances to water treatment [23]. Silver salt precursors are used in this technique to produce ionic silver, which can be reduced and precipitated to form nanoparticles. Some of them includes silver nitrate, silver thiosulphate [Ag(S$_2$O$_3$)23$^-$], diamine silver[Ag(NH$_3$)2$^+$]. The dominant use of Silver Nitrate is attributed to its low cost and chemical stability when compared to other types of silver salts [24]. Usually, the leaf extracts are preferred for the synthesis of AgNPs. Jain et al. reported the synthesis from fruit extracts for the first time [25]. Many plants can actively uptake and reduce metal ions from soils and solutions during the detoxification process, thus forming insoluble complexes with the metal ion in the form of nanoparticles. The AgNPs were stable and had different shapes, such as spheres, trapezoids, prisms and rods, completely dependent on the synthesis mode and conditions applied. Mantion et al. had reported that the sulfur content is responsible for the size and shape i.e., the interaction between the silver ions and thioether moiety of the peptide [26]. The main principle for the synthesis of AgNPs is the metal ion which is in oxidized state will get reduced by the plant material there by converting Ag$^+$ ion into Ag^0 ions. In according to the literature, In *Helianthus annus*, The polyol components and the water soluble heterocyclic components were mainly responsible for reduction of Ag$^+$ as well as stabilization of NPs [27]. In *Camellia sinensis* (green tea) extract has been used as a reducing and stabilizing agent for the biosynthesis of silver nanoparticles in an aqueous solution in ambient conditions. Besides polysaccharides may also preidicted to be the reason for the stability of the NP's [28]. Flavonone and terpenoid components of neem leaf broth, the reaction of the metal ions is possibly facilitated by reducing sugars and the surface active molecules are being predicted to be the reason for the stabilizing the nanoparticles [2]. Kasthuri et al. had reported that Secondary hydroxyl and carbonyl groups of apiin were responsible for the bioreduction of metal salts [29]. However the exact mechanisms of the plant extract mediated synthesis of nanoparticles is still unanswered.

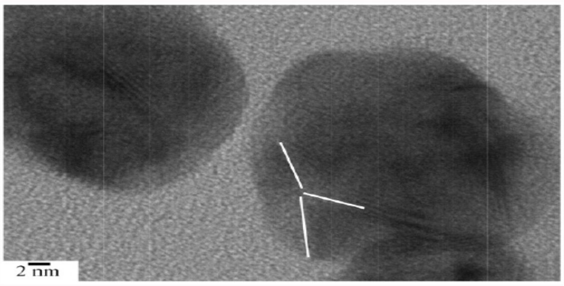

Figure 4: HRTEM representing Higher magnification image of the same area of the Ag particles, illustrating the presence of three-fold twinning in one of them [30].

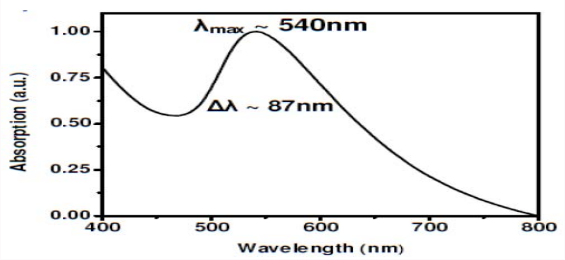

Figure 5: UV-vis absorption spectra of gold nanoparticles [6].

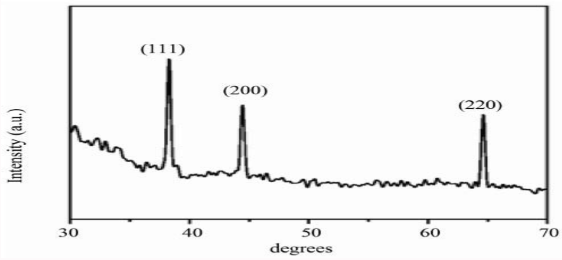

Figure 6: XRD Analysis of AuNPs [6].

Rapid Synthesis of Silver Nanoparticles from Arbutus Unedo (Strawberry) Leaf Extract (An Example)

This was a breakthrough in the field of Bio-nanotechnology in the synthesis of silver nanoparticles just by using two components and had gains nano technologists attention because of its rapidity in the synthesis protocol, easy implementation and low cost. Generally, stabilizing agents are used while in this method such agents were not used thus gained lot of imporatnnce. Kouvaris et al used the leaf extracts and silver nitrate as the materials.

Table 1: Representing several Plants used in the synthesis of Silver synthesis along with their size.

Name of the Plant	Type of Nanoparticle	Size (nm)
Azadirachta indica(Neem)	Ag, Au, and Ag/Au bimetallic	50–100
Aloe vera	Ag	15–20
Emblica officinalis	Ag	20-Oct
Cinnamomum camphora (dried leaf)	Ag	55-80
Tamarind(leaf extract)	Ag	20-40
Carcica papaya	Ag	25-50
Parthenium hysterophorus L	Ag	40-50
Geranium leaves plant extract	Ag	16–40
Alfalfa sprouts	Ag	2–20
Cinnamomum camphora	Ag and Au	55–80
Diopyros kaki	Ag	15-19
Camellia sinensis	Ag	30-40
Eucalyptus hybrid	Ag	50-150
Jatropha curcas(seed)	Ag	15-20
Jatropha curcas (latex)	Ag	20-Oct
Pine apple (leaf extract)	Ag	15-500
Persimmon (leaf extract)	Ag	15-500
Ginkgo (leaf extract)	Ag	*15-500*
Magnolia (leaf extract)	Ag	15-500
Platanus(leaf extract)	Ag	15-500
Azadirachta indica	Ag	20
Hibiscus sabdariffa	Ag	25
Phoma glomerata	Ag	60-80
Cymbopogon flexuosus	Au^0–Ag^0	214.4±4
Anacardium occidentale	Au^0–Ag^0	<10
Rice paper plant stem	Ag	<100

Synthesis

Fresh *Arbutus Unedo* leaves (10g) were taken and mixed with 100ml of distilled water at room temperature. Aqueous solution of 1mM $AgNO_3$ with 50ml of distilled water was prepared at room temperature. The obtained solution was mixed with 50ml of leaf extract at 80°C and magnetically stirred at 1000rpm for 30 seconds.

Results and discussion

UV-vis spectral analysis, TEM analysis was done for the identification of the presence, size, shape of AgNPs. The formation of reddish yellow indicates the formation of silver nanoparticles.

UV-vis results had shown high absorption bands at 436nm. As metal NPs have free electrons, the combined vibration of electrons gives the Surface Plasmon Reasonance (SPR). The intensity of the absorption is directly proportional to the time period of aqueous component. There is change in the color soon after the formation of the nanoparticles because of the excitation of the surface Plasmon reasonance in the formed nanoparticles (Figure 2).

Transmission Electron Microscopy (TEM) analysis reported the formation of nanocrystalline AgNPs with spherical shape. Often agglomeration is also seen with 5-6 NPs. Smaller aggregates were coated with a thin organic layer which acts as a capping agent. Mostly Uniform size of 30nm was found. However, very low level of higher size particles was also found. The Selected Area Diffraction (SAD) pattern detected the crystallinity of AgNPs. The appearance of discrete spots in the ring pattern proved majority of the particles are single crystalline materials and they are oriented along their Ag direction as seen in face centered cubic crystal lattice of silver. High Resolution Transmission Electron Microscopy (HRTEM) had shown to possess the three fold twinning and further proves the single crystalline nature of the particles (Figure 3 and 4).

The color development does not have any correlation with the increase in the absorbance exhibited by nanometal synthesized. The difference in the size morphology has difference in the optical properties. However, researchers are trying to accomplish such implementations for generating such simple, most effective with high yield production which is quiet beneficial for large production for various applications [30] (Table 1).

Production of Gold Nanoparticles

Gardea et al. reported the first gold nanoparticles synthesized, ranges from 2 to 20 nm in size from alfalfa seedlings [31]. Due to the multifunctional activities of AuNPs it is been focused by many research groups. Gold nanoparticles has found its immense applications in diverse fields like chemistry, electronics, medicine and biotechnology due to distinct optical, thermal, catalytic and extraordinary chemical, physical properties. In the field of Biology it's mainly applied for the drug delivery, Bioimaging, DNA labeling etc because of its Biocompatibility. The synthesis of AuNPs can be synthesized by Biological, Physical, chemical methods. In the Biological methods the AuNPs can be formed by reducing Au(III) to Au(0) by using the reducing agents which act on the aldoses and ketones. Mostly the aqueous chloroauric acid is used as the reducing agent. The gold nanoparticles possess different shapes and sizes which depend on the biological species. Shankar et al. reported similar protocol was performed for lemon grass and germanium plant for gold nanoparticle synthesis which is simplest and done at the room temperature, there is a high percentage of thin, flat, and single-crystalline Au nanotriangles and rod shaped structures [32-34]. The Nanotriangles obtained in this method are liquid like. The fluidity occurred due to nanoparticle surface complexation of aldehydes or ketones present in the lemongrass plant. Not only has the biological extract from which it was extracted besides the part of the plant also had its influence on shape. It was reported that root and stem broth of germanium plant had shown to exhibit a high propensity towards forming flat nanostructures and the spherical nanoparticles respectively [35]. Upon incubation of *Triticum aestivum* biomass with Au(III) at different pH of 2.0-6.0, nanostructures of various morphologies were formed such as tetrahedral, decahedral, hexagonal, icosahedral, multitwinned, rod shaped and some irregular shapes. All these nanostructures exhibited face centered cubic lattice geometry with the particle size ranging from 10 to 30 nm. The functional groups of the cell wall are responsible for reduction of gold NPs. This was the first report that anisotrophic gold nanoparticles like truncated icosahedral and rod shaped morphologies were synthesized by agricultural byproduct [36]. As plants cannot be directly uptake gold, so chelating agents like cyanide, iodide, bromide and thiosulphate have been examined in gold accumulation. In *Brassica juncea*, ammonium thiocyanate was used as solubilizing agent, which induced the gold accumulation upto 57µg/g. *Brassica juncea* and *Berkheya coddii* are referred to as hyperaccumulators of gold intracellularly, when sodium thiocyanate

Table 2: Representing the plants used for the synthesis of Gold Nanoparticles with their Sizes.

Plant name	Type of nanoparticles	Size (nm)
Cymbopogon flexuosus plant extract	Au	200-500
Avena sativa (Oat)	Au	May-85
Aloe vera	Au	50-350
Sesbania Drummondii	Au	20-Jun
Avena sativa	Au	5-20 and 25- 85 (depending on pH)
Medicago sativa	Au	20-Feb
Medicago sativa	Au	20-100 (depending on pH)
Cinnamomum Camphora	Au and Ag	55-80
Medicago sativa	Eu-Au Bimetallic	Feb-30
Emblica Officinalis (Fruit)	Au	15-25
Tamarind leaf	Au	20-40
Brassica juncea	Au	May-50
Chilopsis linearis	Au	1.1
Pelargonium graveolens Leaf	Au	20-40
Pelargonium graveolens Stem	Au	8.3–23.8 nm
Pelargonium graveolens Root	Au	11.4–34 nm
Azadirachta indica	Au	50-35
Coriandrum sativum	Au	20.6±7.09
Coleus amboinicus	Au	4.6-55.1
Eucalyptus camaldulensis	Au	1.25-27.5
P. roseum Leaf	Au	2.5–27.5
Camellia sinensis leaf	Au	40
Lawsonia inermis	Au	7.5-65
Phyllanthus amarus	Au	18-38
Aloe ferox Leaf	Au	6–35 nm, 4–45 & 50nm
Hibiscus rosa sinensis	Au	`14
Psidium guajava	Au	27±3
Magnolia kobus	Au	5-300
Diopyros kaki	Au	300
Scutellaria barbata	Au	30-May
Tanacetum vulgare	Au	11
Szyygium aromaticum	Au	100-300
Terminalia catappa	Au	21.9
Mucuna pruriens	Au	6–17.7
Musa paradisiacal	Au	300
Beta vulgaris	Au	25,160, 20 (with nanorod, triangular, spherical shapes respectively)
Beta vulgaris	Au	30 (nanowire)
Centella asiatica	Au	9.3–10.9
Sorbus aucuparia	Au	18
Rosa rugosa	Au	11
Chenopodium album	Au	10
Camellia sinensis	Au	~ 20
Olea europium	Au	50-100
Callistemon viminalis	Au	~ 90
Panax ginseng	Au	16.2±3
Stevia rebaudiana	Au	20-Aug
Magnifera indica	Au	17

Ocimum sanctum	Au	30
Murraya koenigii	Au	20
Cinnamomum zeylanicum	Au	25
Anacardium occidentale	Au	6.5, 17
Cicer arietinum	Au	~ 25
Semecarpus anacardium	Au	13-55
Rosa hybrid	Au	10
Eucalyptus camaldulensis	$Au^0–Fe_3O_4$	20-Jun
Brassica juncea	$Au^0–Ag^0–Cu^0$	May-50

solution is added to artificial substrate. Similarly incase of *Brassica juncea* and *chicory* when either of these chelating agents are used like iodide, bromide, cyanide, thiocyanide or thiosulfate solutions to artificial gold substrate then there is increased accumulation of gold in these plants [37,38]. The extract of the plants as well as the addition chelating agent shows its profound effect on the accumulation of gold intracellularly in *Brassica juncea* and *Berkheya coddii*. It was reported that the addition of cyanide to stem and leaf extracts shown enhanced accumulation compared to its roots while roots had shown increased production when cyanate solution is used. Huang et al. reported that as of silver the polyol and water-soluble heterocyclic components are responsible for reduction. In Calotropis procera Latex, it was found that to act as reducing and capping agent for the formation of gold nanoparticles and it was also stated that the functional groups like alcoholic and phenolic groups are responsible for the reduction of gold to gold nanoparticles [39].

Synthesis of Gold Nanoparticles from Allium Cepa (An Example)

10g of fresh thoroughly washed and chopped onion (*Allium cepa*) were taken. Add 40ml of sterile distilled water and was boiled for 15min. 0.2ml of broth was added to 50ml of 10^{-3}M aqueous chloroauric acid ($HAuCl_4$) solution. UV-vis spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) studies were done to analyze the gold nanoparticles.

Results

The reaction of allium cepa with $HAuCl_4$ ions reduces the gold. Vitamin C present in onion is responsible for reduction of Au^{+3} to Au^0 [6]. Soon the formation of nanoparticles cherry yellowish red color is observed. For stabilizing the nanoparticles 2% chitosan solution is added.

UV-vis spectroscopic studies

A strong resonance at 540nm is clearly seen and arises due to the excitation of surface plasmon vibrations in the gold nanoparticles (Figure 5).

XRD analysis

XRD measurements determined the characteristic peaks are observed at 111°, 200°, 220°. The characteristic peaks corresponding to (111), (200), (220) of Au are located at $2\theta=38.29°$, 44.43° and 64.68°, respectively. Along with these peaks there are some small unidentified peaks are also observed. These results say that the formed gold nanoparticles are crystalline (Figure 6).

SEM analysis

Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid, extra solution was removed using a blotting paper and then the film on the SEM grid were allowed to dry by putting it under a mercury lamp for 5min. SEM photograph of gold nanoparticles clearly indicates that in the room temperature synthesized samples the size the average size of the nanoparticles is ~100nm, with spherical and cubic shape [40] (Figure 7 and Table 2).

Figure 7: SEM image of Gold Nanoparticles [40].

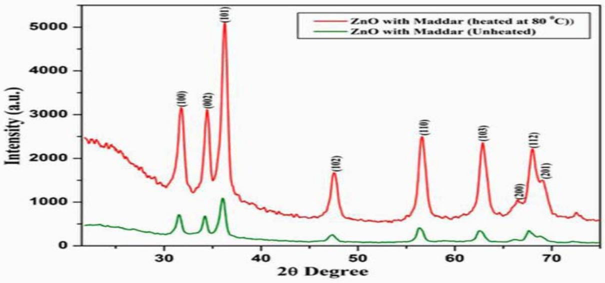

Figure 8: XRD Analysis of ZnO NPs [42,43].

Zinc Oxide Nanoparticles (ZnONPs)

Due to its wide band gap and large exciton-binding energy thereby possessing unique optical and electrical properties and being used for mostly for various applications such as solar cells, UV light-emitting devices, gas sensors, photocatalysts, pharmaceutical and cosmetic industries. Within these days it has gained lot of interest in biomedical applications due to its safe, nontoxicity and Biocompatibility. Hence it is mainly applied in Sunscreens and as a antimicrobial agent. Zinc hyper-accumulators show high metal accumulation capacity, translocation capability which means elemental concentrations in the shoots of a plant should be higher than those in the roots [41], enrichment capability i.e., the concentration ratio of plant shoot to soil should be higher than 1, tolerance capability [42,43]. Qu et al. reported that *Physalis alkekengi* L. is one of the hyper-accumulators of zinc and has high tolerance for zinc in the soil. The chlorophyllin is

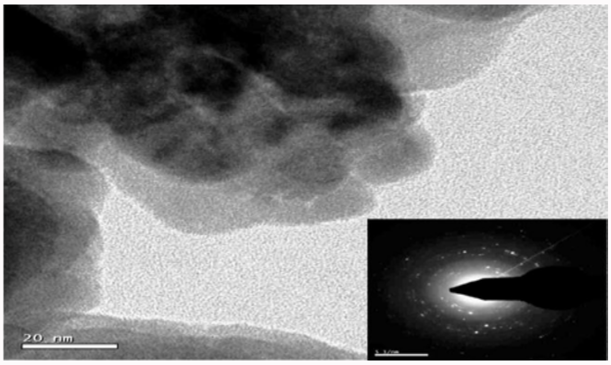

Figure 9: Representing XRD results of TEM image of ZnONPs and the heated and unheated sample inset representing SAED pattern.

responsible for reduction and deposition of zinc oxide Nanoparticles within them. This Zinc hyper accumulator is used to remediate zinc-contaminated soils[44]. Biomedically as of silver Zinc oxide Nanoparticles also show the antimicrobial activity and it was proved from the extracts of plant rhizome of *Alpinia purpurata* [45]. Very recently, using fruit of Citrus aurantifolia extracts, biological and chemical mediated synthesis was reported with Spherical zinc oxide nanoparticles using different concentration of zinc acetate which was used as the zinc source, which is described as the alternative to green procedures [46].

Synthesis of Zinc Oxide Nanoparticles from Calotropis Procera: (An Example)

Calotropis procera acts both as reducing as well as stabilizing agent. The zinc acetate dehydrate, sodium hydroxide and latex of *C. procera* were used as components. 0.02M aqueous solution of zinc acetate dihydrate was added in 50ml of distilled water under vigorous stirring for 10mins. Latex of C. procera was taken of about 0.25, 0.5 and 1.0 ml was added in three set into the above solution. After addition of milky latex, 2M of aqueous NaOH solution was added into the above aqueous solution, resulting in a white aqueous solution at pH 12, and allowed to stir by using magnetic stirrer for 2hr. The precipitate was then taken out and washed repeatedly with distilled water followed by ethanol to remove the impurities for the final products. Then a white powder form was obtained after drying at 60°C in vacuum oven overnight.

Characterisation

The obtained white powder is analyzed for X-ray Diffraction, Transmission Electron Microscope (TEM), Scanning electron microscopy (SEM).

XRD analysis

The X-Ray diffraction (XRD) pattern reveals the formation of ZnO nanoparticles, which shows crystallinity. The XRD patterns of both heated and non-heated ZnO NPs powder embedded in calotropis matrix synthesized by co-precipitation method are reported. When compare the both the samples, XRD Spectra showed strong diffraction peaks at 31, 34, 36, 47, 56, 62, 66, 67 and 68 degrees of 2θ which corresponds to (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes. XRD peaks of heated sample were not as sharp as in the case of non-heated as-prepared ZnO sample. It means that there is slight decrease in crystallinity, which suggests the formation of smaller particle size (Figures 8 and 9).

Table 3: Representing various Nanoparticles synthesized from various plants with their shapes.

Plant Name	Type of nanoparticle	Size (nm)
Medicago sativa (Leaf)	Ti/Ni bimetallic	6-Feb
Medicago sativa (Plant)	Ti/Ni bimetallic	1–4 nm
Medicago sativa	Sm	8-Feb
Medicago sativa	Yb	10-Feb
Medicago sativa	Wuestite (Fe0.902O) and Magnetite (Fe_3O_4)	3.1
Phragmites australis	Cu	10-15 A°
Iris pseudacorus	Cu	15-20 A°
Glycine max	Fe_3O_4	8
Medicago sativa	Lu_2O_3	5-Feb
Aloe barbadensis	In_2O_3	May-50
Solanum lycopersicum	$PbWO_4$	45-55
Medicago sativa	Zinc	2-5.6

TEM analysis

The obtained powder was mixed with the ethanol and dropped on the copper grid and analyzed. TEM analysis reports ZnONPs with average size of 5-40 nm. Selective area electron diffraction (SAED) pattern represents a set of rings containing spots suggesting that nanoparticles have a larger grain size, uniform shape and polycrystalline in nature.

SEM analysis

The morphology of ZnO NPs embedded in calotropis matrix with average particles size and shape in the range of 5-40 nm. Scanning electron microscopy (SEM) image reveals that the particles are of spherical and granular nanosized in nature as depicted. Little agglomeration having sizes about 5nm throughout the carbon coated copper grid was found.

UV-vis spectroscopic studies: The results reported that there was absorption in the ultraviolet band between 200-400 nm. The absorption wavelength at about 368nm of ZnO suggested the excitonic character at room temperature [47].

Simultaneous Synthesis of Gold, Silver and Platinum Nanoparticles using Cochlospermum Gossypium

This gum is an economical source of biosorbent for bioremediation of toxic metal ions and as a matrix for drug disposition with relevance in pharmaceutical field. Natural gums could act as nontoxic vehicles, to stabilize and deliver Nanoparticles for in vivo applications. Cochlospermum gossypium (gum kondagogu) is a plant-derived biotemplate for synthesizing nanoparticles of noble metals. The fresh, clean samples with no extraneous material were used for the synthesis of nanoparticles. GK was powdered in a high-speed mechanical blender and later sieved using a bin (mesh size with 250µm) for fine and uniform sized sample. This powder (2g) was accurately weighed and dispensed into a clean glass beaker containing 1L of deionized water. The whole gum solution was kept on a magnetic stirrer at room temperature and gently stirred over night. Later, the gum solution was allowed to stand at room temperature (30°C) for 12 hours, so as to separate any undissolved matter, the gum solution was filtered. The clear solution so obtained was freeze-dried and stored, until further use. For the preparation of three different noble nanopartiles, a 100µL aliquot of 10mM solutions of $AgNO_3$, $HAuCl_4$ and H_2PtCl_6 were added to 10mL of aqueous solution of plant extract solution. The acidic or basic pH of the colloidal solution was maintained by appropriately adding 0.1N HCl or 0.1N NaOH. All the solution components were purged with nitrogen and reduction proceeded in the presence of nitrogen.

Synthesis of Ag nanoparticles

In this, the mixture containing $AgNO_3$ and plant extract solution was kept for agitation in an orbital shaker, maintained at 45°C, pH 5.0 and at 250rpm for 1h. The color of the solution turned into light yellow after 1h indicating the formation of Ag nanoparticles.

Synthesis of Au nanoparticles

In this, the mixture containing $HAuCl_4$ and plant extract solution was kept at pH 10.0, 75°C at 250rpm for 1h in an orbital shaker. The solution turned into wine red color after 1h, indicating the formation of Au nanoparticles. The addition of NaOH facilitates the opening of the glucose ring by the abstraction of the α-proton of the sugar ring oxygen and metal ions oxidize glucose to gluconic acid there by the color formation occurs.

Synthesis of Pt nanoparticles

The flask containing H_2PtCl_6 and plant extract solution was autoclaved at 15 psi for 15min. The solution turned into dark color, indicating the formation of Pt nanoparticles. The reduction and formation of nanoparticles occurs at a pH of 8.0 and at a temperature of 120°C. The color change in all the three is due to the excitation of surface plasmon vibrations in the formed nanoparticles. There is no aggregation or precipitation of noble metal particles in the solution was observed for prolonged period (>6 months), suggesting that the Cochlospermum gossypium provides an excellent protective environment for the metal hydrosols during their growth process. Generally for the generation of nanoparticles of gold, silver or its alloy reducing agent like glucose is required but using this plant extract there is no need of reducing agent as it selves acts as reducing and capping agent. UV-vis spectroscopic analysis, had shown the surface Plasmon reasonance at 412, 512nm with gold and silver respectively while platinum doesnot show any SPR. Upon ageing with Ag for 12h, SPR band was found to be at 435nm, which means slow processing for extracellular reduction of Ag^+ ions. XRD results has shown a mean size of 2-10 nm of all the three metal Nanoparticles. TEM results reported spherical shaped morphology, with 5.5±2.5nm, 7.8±2.3nm, 2.4±0.7nm respectively for Au, Ag, Pt. FTIR spectra was done for analyzing the molecule responsible for the reduction of metal ion into metal nanoparticle. The plant extract contains aminoacids, fatty acids, sugars etc in them, however there will be specific moiety responsible. The carboxylic groups, hydroxyl groups, Aliphatic and aromatic amines of amino acids are responsible for respective degradation and accumulation of metal ions with respect to Au, Ag and Pt Nanoparticles [48] (Table 3).

Conclusion

Over the past few decades, nanoparticles of noble metals and certain metal oxides such as silver and zinc oxide respectively had exhibited significantly distinct physical, chemical and biological properties from their bulk counterparts. Nano-size particles of less than 100nm in diameter are currently attracting increasing attention for the wide range of new applications in various fields of industry. Although there are several synthesis modes, what so ever, the best mode is biosynthesis which is dependent on the Phytomining and Biosilicification. These processes describes the ultimate reducing agent is plant itself. However, it is still unanswered which biomolecule is responsible for the reduction of metals into nanoparticle. There are few processes in the synthesis of metal Nanoparticles which were rapid without any toxicity just by using two components as of silver. Apart from this synthesis of other important nanoparticles like gold, zinc oxide and simultaneous synthesis of gold, silver and platinum is also described. The reported plants for the synthesis of various nanoparticles and their respective sizes were also described.

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