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Plants: Emerging as Nanofactories towards Facile Route in Synthesis of Nanoparticles

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ABSTRACT

Plant mediated nanoparticles' synthesis has led to a remarkable progress via unfolding a green synthesis protocol towards nanoparticles' synthesis. It seems to have drawn quite an unequivocal attention with a view of reformulating the novel strategies as alternatives for popular conventional methods. Hence, the present review summarizes the literature reported thus far and envisions towards plants as emerging sources of nanofactories.

Introduction

Nanotechnology is an interdisciplinary area of science which has been burgeoning interest across the globe with huge momentum to usher in forming nano revolution. An important area in nanotechnology deals with the synthesis of nanoparticles which has encountered immense progress due to innumerable applications in recent decades.[1] Nanoparticles are particles less than 100 nm in diameter that exhibit new and enhanced size-dependent properties compared to its bulk material.[2] The recent development and implementation of advance technologies have emerged the nano-revolution which provides the tools and technology as platforms for the investigation of biological entities which offer inspiration models for bio-assembled components toward synthesis of nanoparticles. Biosynthesis of nanoparticles is a type of bottom up approach which employs a biological system or its components for the formation of nanoparticles, where the main reaction is reduction of raw metal into nanoparticles. The process of biological route is due to metal tolerance of biological entities.[3] Biological entities in synthesis of nanoparticles may vary from simple prokaryotic bacteria to eukaryotes such as fungi and plants. Compared to microorganisms, plants have better advantages wherein plant mediated synthesis is a one-step protocol towards synthesis whereas microorganisms during the course of time may lose their ability to synthesize nanoparticles due to mutations. Further preservation of microorganisms and maintenance of cultures in active form are very laborious and time consuming. While in plants it is easy and safe with one step protocol towards synthesis; hence research on plants has expanded rapidly.[4,5] The use of plants in synthesis of nanoparticles has become one of the popular alternatives for conventional methods. In recent years, epoch research on plants has gone through the remarkable progress with current upsurge in plant research in synthesis of nanoparticles with controlled size and shape. It is a well-known natural phenomenon of heavy metal tolerance by plants which has resulted in phytomining and phytoremediation. Thus, these unique properties of metal tolerance by plants have been exploited with respect to nanoparticles' synthesis.[6] Plant mediated synthesis of nanoparticles is conferred due to the presence of biomolecules such as proteins, amino acids, vitamins, polysaccharides, polyphenols, terpeniods, and organic acids such as citrates etc. present in the plants as their phyto chemicals. Apart from mediating the synthesis, these molecules also stabilize the nanoparticles formed with desired size and shape. Studies have indicated that biomolecules not only play a role in reducing the ions to the nanosize, but also play an important role in the capping of nanoparticles.[7,8]

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Plant mediated biosynthesis of nanoparticles

The first report of the plant employed in the synthesis of nanoparticles is attributed to *Medicago sativa* (alfalfa) which was capable of synthesizing gold and silver nanoparticles.[9] Since then, more attention has been scattered on plants. Table 1 represents myriad plant species capable of synthesizing nanoparticles. Most of the studies confer the production of nanoparticles by plants that were known to be stable than nanoparticles synthesized by microorganisms.[6] The production of nanoparticles by plants relays on various factors among which, type of processing with optimized parameters is very much essential towards synthesis of nanoparticles such as growing plant in a media incorporated with raw material for the synthesis of nanoparticles, use of dried powdered plant material which is employed in the synthesis of plant material, drying plant material and evaluating nanoparticles synthesis, and employing fruits and flowers in the synthesis of nanoparticles.These different types of processing are known to influence nanoparticles' formation which has been reported in the various literature. When *Pelargonium graveolens* was evaluated for synthesis, reduction of the auric chloride nearly completed within 60 min and the particles' size ranged between 20–40 nm with predominant decahedral and icosahedral in shape. The study also highlighted that functional groups such as positive amino groups, sulfhydryl groups and carboxylic groups were responsible for formation of nanoparticles.[10] Similarly, green unripe *Carica papaya* L fruits upon challenging with 1 mM aqueous solution of silver nitrate, resulted in synthesis of silver nanoparticles within 4 hours of incubation which was confirmed with absorption of spectra of silver nanoparticles formed in the reaction media at 450 nm, which was later confirmed by the characteristic peaks observed in the XRD. The structural view under the scanning electron microscope with average size of the particles synthesized was around 15 nm.[11] Similarly, *Cinnamon zeylanicum* bark extract upon evaluation for synthesis resulted in cubic and hexagonal silver nanocrystals with size ranging between 31–40 nm.[12] *Magnolia kobus*, upon evaluation, was capable of producing stable silver nanoparticles with average particle size ranging from 15 to 500 nm, extracellularly. The study also conferred that the rate of synthesis of the nanoparticles was related to the reaction and incubation temperature. They reported that increased temperature levels allowed nanoparticle growth at a faster rate. Moreover, by increasing the temperature and leaf broth concentrations, size of nanoparticles was reduced. Fourier transformed infrared spectroscopy (FTIR) analysis has shown that gold nanoparticles produced by *Magnolia kobus* extract were surrounded by proteins and other biomolecules such as terpenoids having functional groups of amines, aldehydes, carboxylic acid, and alcohols which play a vital role in synthesis of nanoparticles.[13]

It was also reported that phyllanthin extract synthesized anisotropic gold and spherical–quasi-spherical silver nanoparticles by reducing aqueous chloroauric acid and silver nitrate solution at room temperature. The size and shape of the nanoparticles can be controlled by varying the concentration of phyllanthin extract to tune their optical properties in the near-infrared region of the electromagnetic spectrum. The case of low concentration of the extract with gold chloroaurate offers a slow reduction rate along with the aid of electron-donating group containing the extract leading to formation of hexagonal or triangular-shaped gold nanoparticles.[57] *Camellia sinensis* extract was evaluated to synthesize gold nanoparticles and silver nanostructures in aqueous solution. The study conferred biomolecules present in *Camellia sinensis* extract which were responsible for production and stabilization of silver and gold nanoparticles, suggested that caffeine and theophylline present in tea extracts might be responsible for catalysis and synthesis of nanoparticles. Black tea leaf extract challenged with silver nitrate and gold chloro aurate resulted in the production of polydispersed silver and gold

Table 1. Synthesis of nanoparticles using plants

Silver nanoparticles synthesizing plants	
Acalypha indica[14]	*Euphorbia hirta*[29]
Artocarpus Heterophyllus[15]	*Ficus bengalensis*[30]
Boswellia ovalifoliolata[16]	*Fissidens minutes*[31]
Brassica juncea[17]	*Gliricidia sepium*[32]
Cardiospermum helicacabum[18]	*Honey*[33]
Cassia fistula[19]	*Ipomoea aquatic*[34]
Cassia occidentalis[20]	*Moringa oleifera*[35]
Catharanthus roseus[21]	*Nelumbo nucifera*[36]
Citrus Sinensis[22]	*Opuntia ficus-indica*[37]
Clerodendrum inerme[23]	*Parthenium hysterophorus*[38]
Cochlospermum gossypium[24]	*Syzygium cumini*[39]
Coriandrum Sativum[25]	*Tanacetum vulgare*[40]
Datura metel[26]	*Tribulus terrestris*[41]
Desmodium triflorum[27]	*Trichoderma koningii*[42]
Eucalyptus hybrid[28]	*Zea mays*[43]
Gold nanoparticles synthesizing plants	
Camellia sinensis[44]	*Psidium guajava*[50]
Coriandrum sativum[45]	*Scutellaria barbata*[51]
Cymbopogon flexuosus[46]	*Syzygium aromaticum*[52]
Momordica charantia[47]	*Tamarindus indica*[53]
Mucuna pruriens[48]	*Terminalia catappa*[54]
Ocimum basilicum[49]	
Gold and Silver nanoparticles synthesizing plants	
Aloe vera[55]	*Emblica officianalis*[59]
Azadirachta indica[56]	*Emblica officinalis*[60]
Apiin (henna leaves)[57]	*Murraya koenigii*[61]
Cinnamomum camphora[58]	

nanoparticles which were found to be stable. The study also reports polyphenols and flavonoids were responsible for synthesis of nanoparticles.[44] Furthermore, Hudlikara *et al*. reported synthesis of titanium dioxide nanoparticles with 0.3% aqueous extract prepared from latex of *Jatropha curcas* L, with nanoparticles' size within the range of 25-100 nm. Fourier Transform Infrared Spectroscopy was performed to find the role of curcain, cyclic peptides, namely curcacycline A and curcacycline B as possible reducing and capping agents.[62] The leaf extract of *Ocimum sanctum* rapidly synthesized silver nanoparticles with a size range of 4–30 nm within 8 min of reaction time. It was reported that *Ocimum sanctum* leaf extract could reduce silver ions into crystalline silver nanoparticles ranging 4–30 nm within 8 min of reaction time. These nanoparticles were stable due to the presence of proteins which may act as a capping agent. Biosynthesized silver nanoparticles have also displayed strong antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*.[63] A green synthesis route for the production of silver nanoparticles using methanol extract from *Solanum xanthocarpum* berry was reported; the reduction was rapid within 25 min at 45^{o}C. The synthesized silver nanoparticles were characterized using UV–Visible spectrophotometry, powdered X-ray diffraction, and transmission electron microscopy. The nanoparticles were found to be about 10 nm in size, mono-dispersed in nature, and spherical in shape.[64] Hence, the brief reports discussed above have given an insight towards plant mediated nanoparticles' synthesis wherein the biomolecules present in plants were held responsible for synthesis of nanoparticles due to which there is an burgeoning interest across the globe for evaluating plants for synthesis of nanoparticles and thus such processes form a safer alternative and eco friendly. At the same time, few studies also confer and report that various parameters attribute to the size control synthesis of nanoparticles.

Factors influencing the nanoparticles' synthesis

Several factors such as temperature, pH, concentration of extracts, concentration of raw material, etc. influence the reduction process of metal ions into the metal nanoparticles.

pH

The pH value of the medium influences the size of nanoparticles under formation in both extracts and living plants. Studies by Gardea Torresdey *et al*. on alfalfa biomass indicated that pH is an important factor in the bioformation of colloidal gold.[65] Similarly, formation of gold nanoparticles was evaluated using biomass of *Avena sativa*. The study also reported that the size of gold nanoparticles can be controlled by altering the pH of medium.[66]

Temperature

One of the most interesting aspects of nanoparticles' biosynthesis is the fact that this process occurs at ambient temperature. However, the temperature of the reaction medium is a critical factor that determines the nature of nanoparticles formed. When *Cymbopogon flexuosus* was evaluated to produce gold nanoparticles at higher temperatures, the percentage of gold nanotriangles relative to spherical particles were significantly reduced at high temperature, whereas low temperature mostly promoted nano triangle formation.[67]

Biomolecules

Among the various categories of compounds synthesized by plants such as phytochemicals, primary and secondary metabolites are known as important natural resources for the synthesis of metallic nanoparticles.[68] A large number of papers have been published on the biosynthesis of nanoparticles using the phytochemicals contained in the extracts of a number of plant species. On the contrary, little has been understood about this process in living plants. Beattie and Haverkamp recently investigated gold and silver nanoparticles formation within the tissues of *Brassica juncea* with the aim of clarifying the mechanisms of nanoparticle formation and a couple of experimental observations were recorded. It was found that the sites of the most abundant reduction of metal salts to nanoparticles were the chloroplasts in which high reducing sugars (glucose and fructose) are responsible for biofabrication of silver and gold nanoparticles.[69]

Purification of nanoparticles

Purification of nanoparticles is carried out by an array of techniques such as centrifugation, which forms a base for nanoparticle separation wherein nanoparticles which are denser than a liquid settle down due to the gravitational force.[70] Usually ultra centrifugation techniques are widely used to separate the nanoparticles based on the size and shape. Apart from centrifugation technique, chromatographic based separation is followed in order to separate nanoparticles based on the coefficients between mobile phase and stationary phase. Use of HPLC has been reported in the various literature from which ion exchange chromatographic separation is followed during which, based on the charge, nanoparticles are separated from the mixture.[71] The efficient separation process for nanoparticles are attributed to one or more techniques for instance extraction of nanoparticles based on their solubilities in two different miscible liquid phases usually water and organic solvents, which is followed by chromatographic techniques or electrophoresis techniques. Electrophoresis techniques employ the uniform electric charge for separation wherein charge particles migrate towards the opposite electrode based on the size and shape of the nanoparticles.[72] Separation of nanoparticles is an important aspect for the application of nanoparticles.[73]

Applications of plant mediated nanoparticles

Green principle based synthesized nanoparticles are known to have immense applications in the field of medicine and biology when compared to the nanoparticles synthesized by chemical protocols which involves the use of harsh solvents or surfactants. The reducing agents in chemical synthesis are known to generate hazardous waste but in green principle based nanoparticles, no use of hazardous chemicals instead of phyto biomolecules present in the plants form the reducing agents and stabilizing agents which typically increase the biomedical applications of green principle based nanoparticles. *In viv*o applications of the plant mediated nanoparticles are more superior compared to the chemically synthesized nanoparticles due to the fact that the biomolecules such as amino acid, proteins, salts and so forth, which are responsible for synthesis and stability of nanoparticles upon evaluation at *in vivo* condition, cause irreversible agglomeration due to chemical similarity among the cellular growth components which are required for cell growth and proliferation.[74] Some studies also suggest that use of plant mediated synthesized nanoparticles are more ideal and compatible for their use in nanomedicine because of their stability in various biological media.[75] Plant mediated nanoparticles are evaluated as potent antimicrobial agents against various human and phytopathogenic microorganisms. Biosynthesized silver nanoparticles using stem bark extracts of Boswellia were evaluated against a panel of pathogenic microorganisms viz *Proteus, Pseudomonas, Klebsiella, Bacillus* and *E.coli* species of bacteria and *Aspergillus*, *Fusarium, Curvularia* and *Rhizopus* species of fungi.[76]

Nanoparticles synthesized via plants, are also employed in physio-chemical applications; for instance, Indium oxide nanoparticles using *Aloe vera* plant displayed a strong photoluminescence in the UV region. The strong emissions of indium oxide are attributed to the radioactive recombination of electron occupying oxygen vacancies with a photo-excited hole. Thus, the study has conferred the use of plant mediated nanoparticles as fluorescence labels towards detection of various analytes.[77]

Characterization of plant mediated nanoparticles and their applications

Characterization of nanoparticles is one of the important aspects which are carried out by microscopic techniques such as scanning electron microscopy, transmission electron microscopy and atomic force microscopy. These microscopic techniques are employed to reveal the size and shape of nanoparticles as described in the literature reported pertaining to nanoparticle synthesis. Initially, preliminary confirmation of nanoparticles is carried out by UV-Visible spectroscopic technique which represents different characteristic peaks at absorptions at electromagnetic spectrum which is due to the surface plasma resonance of the nanoparticles formed. Further characterization of nanoparticles is carried out with analytical hyphenated techniques such as fourier transform infrared (FTIR) spectroscopy which measures infrared intensity versus wavelength of light which results in determination of associated biomolecules of plants with nanoparticles. Apart from these techniques, XRD and Raman spectroscopy are widely used to characterize the nanoparticles formed.[78] The fate of nanoparticles mainly depends on the characterization which reveals the size, shape and nature of the nanoparticles.

Future prospective

Plant mediated nanoparticles' synthesis protocols have an upsurge in recent past as a safe, eco-friendly and an alternative for most popular conventional methods which are bound with various implications. Promoting biosynthesis of nanoparticles can influence the commercial applications of these nanoparticles in the field of pharmaceuticals and other medical sciences which are limited factors for nanoparticles synthesized via conventional methods. The present review summarizes the literature, which confers plants as emerging source for nanoparticle synthesis, which can be advantageous over other biological processes such as microorganism by eliminating the elaborate process of maintaining microorganism cultures which can lose its potential to synthesize due to mutations. At the same time, harvesting the endangered plant species may pose a risk among the plant diversity which can form a major impact. Hence, in this regard new technologies offer isolation of biomolecules responsible for synthesis of nanoparticles and challenge synthesizing the nanoparticles forming template based synthesis of nanoparticles. In the near future, a thorough detailed study will be valuable enough to give a clear description of biomolecules mediating the synthesis of nanoparticles which will influence the rate of synthesis and improve properties of nanoparticles with stability.

Conclusion

Increasing awareness towards green chemistry and biological processes has led to desire and influenced process which is environment-friendly for the synthesis of non-toxic nanoparticles. Owing to the rich biodiversity of plants, mediated nanoparticle synthesis has become a subject of interest across the globe with different plant species being rapidly explored and evaluated for synthesizing of nanoparticles. Nanoparticles synthesized via plants have been used for human benefit. The mechanism of plants in synthesizing nanoparticles is yet to be completely elucidated. Additional research in this area can further increase the potential in biosynthesis of nanoparticles. Harvest of endangered species of plants may pose a risk to the biodiversity of plant kingdom which should be looked forward in the near future. Future research on plant mediated biological synthesis of nanoparticles with unique optoelectronics, physicochemical and electronic properties are of great importance for applications in the areas of chemistry, electronics, medicine and agriculture.

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The authors declare no ethical issues.

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