Green Chemistry Approach of Metal Nanoparticles Synthesis

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***Abstract*- Nanoparticles are being viewed as fundamental building blocks of nanotechnology. They are the starting point for preparing many nanostructured materials and devices. These particles having at least one dimension of less than 100 nm. Synthesis of nanoparticles is an important component of rapidly growing research efforts. The nanoparticles of a wide range of materials can be prepared by numerous methods like chemical, physical and biological methods. The physical and chemical methods have been widely used to synthesize nanoparticles of varying size and shapes. The important criterion in these methods of synthesis was expensive and since it often requires extremes of temperature, pressure and energy. The chemical synthesis protocols employed previously have used toxic chemicals, which can have undesirable side effects in some applications and also environmental concerns. Therefore presently, there is a growing need to synthesize the nanoparticles in a cost effective and safe way. The exploitation of biological systems emerged as a novel method for the synthesis of nanoparticles in this regard.**

***Keywords*: Green approach, Biosynthesis, Metal Nanoparticles, Reduction, Plants**

Introduction

Nanobiotechnology deals with the synthesis of nanostructure using living organisms. Biosynthesis is not only a good way to fabricate benign nanostructure materials, but also to reduce the use or generation of hazardous substances to human health and the environment. This approach provides a facile and convenient entry for producing multiple inorganic nanoparticles. As a result, researchers in the field of nanoparticle synthesis and assembly have turned to biological systems for inspiration. Recently, biosynthesis methods employing either microorganisms or plants or their extracts have emerged as a simple and viable alternative to chemical and physical synthesis procedures [4]. Biological method can be divided into two categories depending on the place where the nanoparticles or nanostructures are created either intra or extra cellularly by both organisms and plants [10].

Synthesis of Nanoparticles

Among the use of living organisms for nanoparticle synthesis, plants have found application particularly in metal nanoparticle synthesis. Use of plants and plant parts for synthesis of nanoparticles could be advantageous over other environmentally benign biological processes as this eliminates the elaborate process for maintaining the cell cultures. Biosynthesis process for nanoparticles would be more useful if nanoparticles were produced extracellularly using plants or their extracts in a controlled manner according to their size, dispersity and shape. Plant use can also be suitably scaled up for large-scale synthesis of nanoparticles [8]. Synthesis using bio-organisms, especially plants that secrete the functional molecules for the reduction of metal ions, is compatible with the green chemistry principles: the bio-organisms are (i) eco-friendly (ii) reducing agent employed and (iii) capping agent in the reactions [9].

Mechanism of Nanoparticles Synthesis

The mechanism of nanoparticles formation occurs in four stages *viz*., recognition -reduction - limited nucleation and growth [9]. Metal ions were trapped on the surface of proteins in the leaf extract *viz*., electrostatic interactions in the first stage which is known as recognition process. Thereafter, metal ions were reduced by proteins extracted from leaf extract, leading to the changes in the secondary structures of the proteins and formation of metal nuclei, which subsequently grew further by reduction of metal ions and accumulation on these nuclei. The flexible linkage of the proteins and the large numbers of biomolecules ranged in the reaction solutions might have led to the isotropic growth and the formation of the most stable nanoparticles in reaction solution. The schematic representation of nanoparticles formation shown in figure 1.

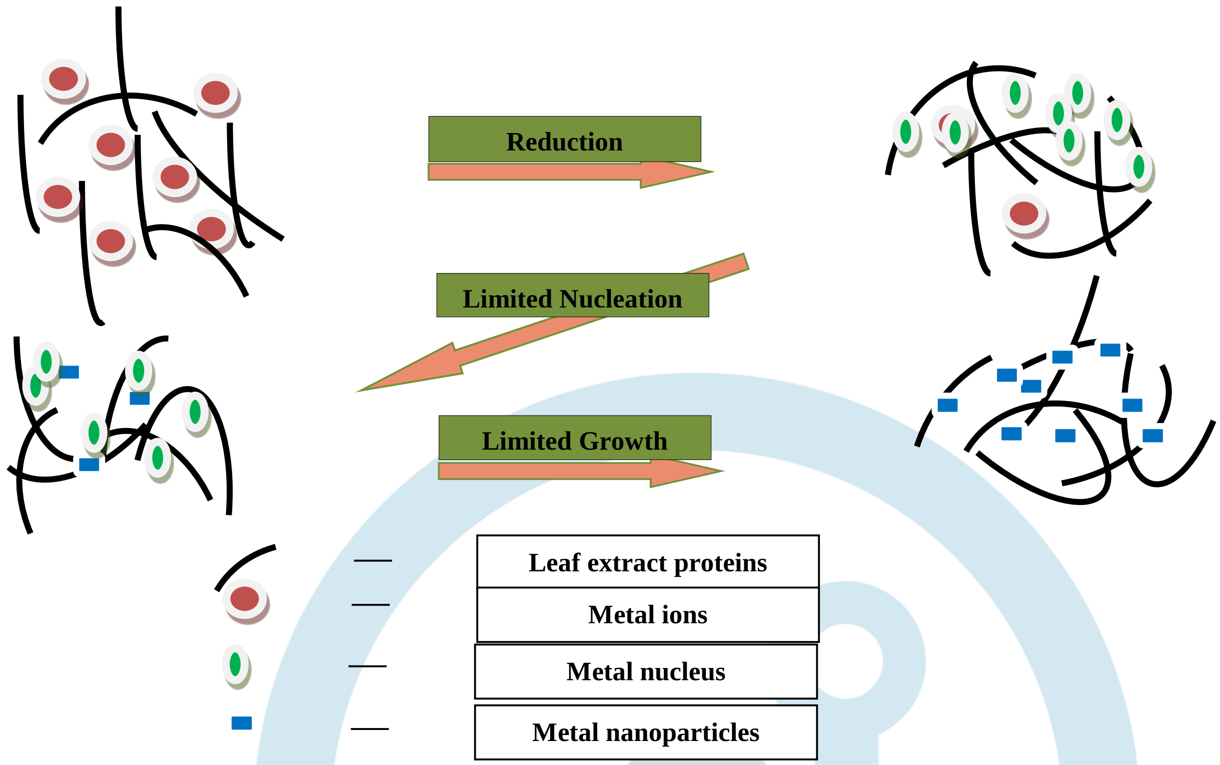

Fig.1. Mechanism of nanoparticle formation by plant

Biogenic Synthesis of Different Nanoparticles by Plants

Several plants have been successfully used for efficient and rapid synthesis of silver, gold and biometallic nanoparticles.

Silver Nanoparticles

Plants or their extracts have been explored in the synthesis of silver nanoparticles using silver ions as substrate. Aqueous silver nitrate solution, after reacting with geranium (*Pelargonium graveolens*) leaf extract, led to rapid formation of highly stable, crystalline silver nanoparticles (16 to 40 nm), which assembled in the reaction medium into quasilinear superstructures. The rate of nanoparticle synthesis was very high, which justifies use of plants over microorganisms in the biosynthesis of metal nanoparticles through greener and safer methods [12]. The silver nanoparticles synthesized by treating silver ions with *Capsicum annuum* L. leaf extract, the crystalline phase of the nanoparticles changed from polycrystalline to single crystalline and their size increased with increasing reaction time. Five hours reaction time led to spherical and polycrystalline shaped nanoparticles (10 ± 2 nm). With increase in reaction time to 9 and 13 h, the size of the nanoparticles was increased to 25 ± 3 nm and 40 ± 5 nm, respectively. Amine groups containing proteins in extract were found to cause the reduction of silver ions, leading to silver nanoparticle synthesis in the solutions [9]. Alfalfa (*Medicago sativa)* plants have been shown to be an efficient synthesis of silver nanoparticles. The roots were capable of absorbing silver from the agar medium and transferring it to the shoot and the silver atoms arrange themselves by undergoing nucleation to form nanoparticles. The nucleated nanoparticles further join to form larger arrangements, suggesting different organization levels [18].

Gold Nanoparticles

Gold nanoparticles have been synthesized by using the chloroaurate ($HAuCl_4$) as a precursor. A small quantity of geranium (*Pelargonium graveolens*) leaf extract was inoculated with an aqueous solution of 1 mM chloroauric acid ($HAuCl_4$) and allowed to react for 2 h. The appearance of a pink-ruby red color indicated gold nanoparticle synthesis. Most probably, the stabilizing/reducing molecules were citronellol and geraniol, which are known to be present in larger concentrations in geranium leaves. This short exposure of leaf extract 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 [13, 14]. The control over shape and size of gold nanoparticles has been achieved in lemongrass (*Cymbopogon flexuosus*). Anisotropic gold nanotriangles have been synthesized by the reaction of lemongrass extract with aqueous gold ions. Size of the gold nanotriangles was controlled by varying the concentration of the lemongrass extract in the reaction medium. With increasing amounts of extract added to the $HAuCl_4$ solution the average size of the triangular and hexagonal particles decreased, while the ratio of the number of spherical nanoparticles to triangular/hexagonal particles increased [16]. Bioreduction of $HAuCl_4$ by tamarind (*Tamarindus indica)* leaf extract led to the formation of flat and thin single crystalline gold nanotriangles with unique and highly anisotropic planar shapes. These may find application in photonics, optoelectronics and optical sensing [1]. Proteins and biomolecules from Bengal gram beans (*Cicer arietinum*) mediate the bioreduction of aqueous gold (III) ions directing the formation of triangular gold prisms. Control of the morphology of gold particles has been achieved by varying compositions of gram bean extract and aqueous gold (III) solution [6]. Alfalfa (*Medicago sativa*) biomass also efficiently reduce gold ions to gold nanoparticles of different types such as face centered cubic (fcc) tetrahedral, hexagonal platelet, icosahedral multiple twinned, decahedral multiple twinned, and irregular shaped particles. Among these, icosahedral and irregular particles were abundant or more frequently formed [5]. The use of ground dry wheat (*Triticum aestivum*) biomass with 0.3 mM potassium tetrachloroaurate solution at various pH values (2 to 6) for 3.5 h caused bioreduction of gold ions, leading to the synthesis of gold nanoparticles (10 to 30 nm). Various shaped nanoparticles have been observed, such as fcc tetrahedral, fcc hexagonal platelets, irregular shaped, rod shaped, decahedral multiple twinned, and icosahedral multiple twinned shapes [2, 3]. Sweet desert willow (*Chilopsis linearis*) has been demonstrated the ability for intracellular gold nanoparticle synthesis. This plant has the capability to take up gold from gold-enriched media (160 mg gold L^{-1} in agar) and synthesized nanoparticles of average size of 8, 35, and 18 Å in root, stem, and leaves, respectively. The average size of the Au nanoparticles formed by various tissues has been found to be related to the concentration of Au accommodated in tissues and their location in the plant [11]. Similarly, growth of *Sesbania* seedlings in chloroaurate solution resulted in the accumulation of gold with the formation of stable gold nanoparticles in plant tissues. Transmission Electron Microscopy (TEM) analysis revealed that the intracellular distribution of monodisperse nanospheres. This study has proposed that reduction of the metal ions was catalyzed by secondary metabolites present in cells [17].

Bimetallic Nanoparticles

In addition to the individual synthesis of either silver or gold nanoparticles, plants have been reported for their potential for both silver and gold nanoparticles synthesis. Neem (*Azadirachta indica*) leaf extract has been used for the extracellular synthesis of pure metallic silver, gold and bimetallic gold/silver nanoparticles. Use of neem leaf extract for nanoparticle synthesis has an advantage in terms of the rapid formation of stable silver and gold nanoparticles at higher concentrations. The silver and gold nanoparticles were polydisperse, with a large percentage of gold particles exhibiting an interesting flat, plate like morphology, while silver nanoparticles formed in the mixtures were spherical, polydisperse and of 5 to 35 nm in diameter. This characteristic of competitive reduction of gold and silver ions by neem leaf extract leads to the synthesis of bimetallic gold core - silver shell nanoparticles ranging in size from 50 to 100 nm [15]. The sun-dried biomass of *Cinnamomum camphora* leaf when incubated with aqueous silver or gold precursors at ambient temperature produces both silver nanoparticles (55 to 80 nm) and triangular or spherical gold nanoparticles. The marked difference in shape of gold and silver nanoparticles could be attributed to the comparative potential of protective and reductive biomolecules from leaves. The polyol and water-soluble heterocyclic components were mainly responsible for the reduction of silver ions or chloroaurate ions [7]. The control over the shape and size of gold and silver nanoparticles has been obtained with the use of *Aloe vera* leaf extract as reducing agent. The extract volume used for the synthesis of nanoparticles and temperature during the reaction had a great impact on the synthesis of characteristic nanoparticles. Different constituents of the extract have been reported to be responsible for the synthesis of single crystalline gold nanotriangles with edge lengths of around 30 nm and spherical silver nanoparticles of size 15.2 ± 4.2 nm [4]. Amla (*Emblica officinalis*), an Indian gooseberry fruit extract, showed potential for extracellular synthesis of gold and silver nanoparticles. Reaction of aqueous silver sulfate and chloroauric acid solutions with *Emblica officinalis* fruit extract leads to rapid reduction of the silver and chloroaurate ions to highly stable silver and gold nanoparticles. TEM images confirmed the formation of silver (10 to 20 nm) and gold (15 to 25 nm) nanoparticles [1]. The plants have also been used for the synthesis of intracellular alloy nanoparticles. Mixed alloy nanoparticles of gold, silver and copper metals showing good specificity and reactivity have been synthesized by living mustard (*Brassica juncea*) plants. The seeds of *Brassica juncea* were sown in soil enriched with gold chloride, silver nitrate and copper chloride solutions. After 14 days growth on such metal ion-enriched soil, the biomass was harvested and dried at 110^0C, then ground and sieved to less than 180 µm. Further, a Scanning Transmission Electron Microscopy-Energy Dispersive X-ray (STEM-EDX) analysis shown that all three elements - gold, silver and copper were present in all the nanoparticles and their size ranged from 5 to 50 nm [17].

Conclusion

The synthesis methods based on naturally occurring biomaterials provide an alternative means for obtaining the nanoparticles. Use of plants in synthesis of nanoparticles is quite novel leading to truly 'green chemistry' route. This green chemistry approach towards the synthesis of nanoparticles has many advantages such as, ease with which the process can be scaled up, economic viability, eco-friendly and safe way to produce nanoparticles.

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