Review Paper

Plants: Green Route for Nanoparticle Synthesis

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Available online at: www.isca.in

Received 8th August 2012, revised 17th August 2012, accepted 3rd September 2012

Abstract

The synthesis of nanoparticles has become the matter of great interest in recent times due to its various advantageous properties and applications in various fields. Though physical and chemical methods are more popular for nanoparticle synthesis, the biogenic production is a better option due to eco-friendliness. This review reports the potential of plants i.e. "green chemistry" to synthesize nanoparticles not only in the laboratory scale but also in their natural environment. Furthermore, factors affecting biosynthesis along with current and future applications are also discussed.

Keywords: Nanoparticles, plants, biosynthesis, applications.

Introduction

Nanoparticle having one or more dimensions of the order of 100nm or less- have attracted considerable attraction due to their unusual and fascinating properties, with various applications, over their bulk counterparts^{1,2}. Currently, a large number of physical, chemical, biological, and hybrid methods are available to synthesize different types of nanoparticles³⁻⁶. Though physical and chemical methods are more popular for nanoparticle synthesis, the use of toxic compounds limits their applications. The development of safe eco-friendly methods for biogenetic production is now of more interest due to simplicity of the procedures and versatility^{7,8}. Due to their amenability to biological functionalization, the biological nanoparticles are finding important applications in the field of medicine⁹. The antimicrobial potential of metal based nanoparticles has led to its incorporation in consumer, health-related and industrial products 10.

Plants-the Green route for biosynthesis of nanoparticles

Nature has devised various processes for the synthesis of nanoand micro- length scaled inorganic materials which have contributed to the development of relatively new and largely unexplored area of research based on the biosynthesis of nanomaterials. Synthesis using bio-organisms is compatible with the green chemistry principles. "Green synthesis" of nanoparticles makes use of environmental friendly, non-toxic and safe reagents. Figure 1 shows the general biosynthesis of metal nanoparticles from biological sources¹¹⁻¹³.

Phytomining is the use of hyper accumulating plants to extract a metal from soil with recovery of the metal from the biomass to return an economic profit¹⁴. Hyper accumulator species have a physiological mechanism that regulates the soil solution concentration of metals. Exudates of metal chelates from root system, for example, will allow increased flux of soluble metal

complexes through the root membranes¹⁵. It has been observed that stress tolerant plants have more capacity to reduce metal ions to the metal nanoparticles¹⁶. Mechanism of biosynthesis of nanoparticles in plants may be associated with phytoremediation concept in plants¹⁷⁻¹⁹. Biosilcification also results in nanoparticles in some higher plants as shown in figure 2²⁰.

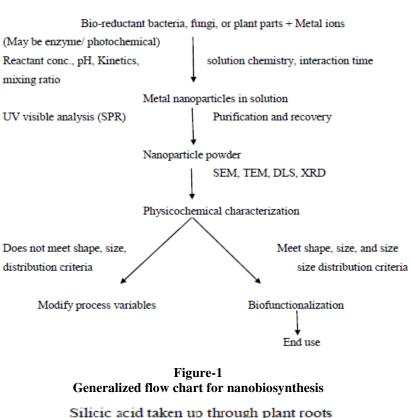
Factors affecting biosynthesis of nanoparticles: Temperature plays an important role to control the aspect ratio and relative amounts of gold nanotriangles and spherical nanoparticles. Temperature variations in reaction conditions results in fine tuning of the shape, size and optical properties of the anisotropic nanoparticles²¹. More than 90% of leaf extracts of two plants-*Magno*lia *kobus* and *Diopyros kaki* was converted to gold nanoparticles at a reaction temperature of 95 °C in few minutes, suggesting reaction rates higher or comparable to those of nanoparticle synthesis by chemical methods²². The size of gold nanoparticles was shown to increase at higher reaction temperatures as explained by an increase in fusion efficiency of micelles which dissipates supersaturation²³.

pH of the medium influence the size of nanoparticles at great concern. For example, the size of gold nanoparticles was controlled by altering the pH of the medium in *Avena sativa*²⁴. The reaction mechanism for the formation of magnetite nano particles have been found to be influenced by pH when coprecipitation method was followed²⁵.

Other than pH and temperature other factors also play role in nanoparticle synthesis. The size and crystallinity of magnetite nanoparticles was found to increase with increasing molar ratios of ferric/ferrous ions during synthesis by hydrothermal synthesis method according to the Schikorr reaction²⁶. The band gap energy was found to decrease with increase in dopant concentration in ZnS samples as determined by optical absorption spectroscopic technique²⁷. The sizes of gold nanoparticles decreases with increasing NaCl concentrations

(size ranges, 5-16 nm) than those synthesized without addition of NaCl (size ranges 11-32 nm)²⁸. Chloride, bromide and iodide affect nanoparticle formation in plants. Chloride promotes growth of nanotriangles while iodide causes distraction in nanotriangle morphology and induces formation of aggregated spherical nanoparticles²⁹. Chloride ion results in the formation of diamond-shaped copper nanoparticles³⁰. Sun-dried biomass of *Cinnamomum camphora* leaf when incubated with

aqueous silver or gold precursors at ambient temperature produces both silver nanoparticles (55–80 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 leaf extracts. The polyol and water-soluble heterocyclic components were mainly responsible for the reduction of silver ions or chloroaurate ions³¹.



Generalized flow chart for nanobiosynthesis

Silicic acid taken up through plant roots

Transport through xylem as silicon complex

Complex reaches stems/leaves

Mineral deposition

Breakdown triggered by change in pH

Release of silicic acid induced

Condensation results in silica

Figure-2 Flowchart for biosilcification process

Nanoparticles synthesized by plants

Nanoparticle biosynthesis is an eco-friendly approach for recovering metals, for example gold, which are catalytically active for reactions and selective oxidation of CO^{32, 33}. Synthesis of mixed nanoparticles alloys having various technological applications and catalysts of specific composition that can't be produced by traditional methods can also be possible. Nanoparticles can be applied in sensors^{34, 35} and medicine i.e. nanomedicine³⁶.

Si-Ge-O nanocomposite by diatoms

Fabrication of Silicon-Germanicum nanoparticles have been reported from freshwater diatom *Stauroneis sp.* ³⁷. Silica from cells of *Nitzschia frustulum*, which possess blue photoluminescence have been cultured in bioreactor whose intensity and wavelength depends on the change in frustules nanostructure ³⁸.

Silver nanoparticles

Silver nanoparticles have attracted intensive research interest because of their important applications in antimicrobial, catalysis, and surface-enhanced Raman scattering³⁹⁻⁴¹. For centuries, silver has been used as an antimicrobial agent. The recent resurgence in interest for this element particularly focuses on the increasing threat of antibiotic resistance, caused by the abuse of antibiotics^{42, 43}.

There are several hypotheses to explain the antibacterial activity of silver nanoparticles. The rapid breakdown of silver nanoparticles releases ionic silver that inactivates vital bacterial enzymes by interacting with essential thiol groups. Silver ions can inhibit bacterial DNA replication, damage bacterial cytoplasm membranes, depleting levels of intracellular adenosine triphosphate (ATP) and finally cause cell death⁴⁴. The high specific surface-to-volume ratio of silver nanoparticles increases their contact with microorganisms, promoting the dissolution of silver ions, thereby improving biocidal effectiveness. The ability of silver nanoparticles to release silver ions is a key to their bactericidal activity⁴⁵. Silver nanoparticles can be synthesized in a number of ways, the borohydride reduction of silver salts being the most common. Stabilization is achieved using capping agents that bind to the nanoparticle surface and improve stability and water solubility, which are essential to prevent aggregation; examples include water-soluble polymers, oligosaccharides and polysaccharides, sodium dodocyl sulphote (SDS) and sophorolipid (glysolipid) 46 dodecyl sulphate (SDS) and sophorolipid (glycolipid)

Silver nanoparticles of 20-30 nm from leaves of *Acalypha indica* showed antimicrobial activity against *E. coli* and *Vibrio cholera*⁴⁷ while silver nanoparticles of 3-12 nm from peels of *Citrus sinensis* have been reported to show activity against *Bacillus subtilis*⁴⁸. Particles of size 33.67 nm from *Allium cepa* stem show antimicrobial activity against *E. coli* and *S. typhimurium*⁴⁹. Silver nanoparticles of size 8 nm from leaves of

Nicotiana tobaccum inhibits Pseudomonas putida, P. vulgaris, Escherichia coli DH5α, B. subtilis, P. aeruginosa and Salmonella typhi⁵⁰.

Gold nanoparticles

Au particles are particularly and extensively exploited in organisms because of their biocompatibility⁵¹. Gold nanoparticles (Au) generally are considered to be biologically inert but can be engineered to possess chemical or photo thermal functionality. On near infrared (NIR) irradiation the Au-based nanomaterials, Au nanospheres, Au nanocages, and Au nanorods with characteristic NIR absorption can destroy cancer cells and bacteria via photo thermal heating. Au-based nanoparticles can be combined with photo sensitizers for photodynamic antimicrobial chemotherapy. Au nanorods conjugated with photo sensitizers can kill MRSA by photodynamic antimicrobial chemotherapy and NIR photo thermal radiation^{52, 53}.

Aggregated forms of nanoparticles like gold nanotriangles have been reported in lemon grass extracts and tamarind leaf extracts⁵⁴ and dead biomass of *Humulus lupulus* also produces gold nanoparticles⁵⁵. Extra cellular synthesis of gold nanoparticles has been observed using *Emblica officinalis* fruit extract as a reducing agent.

Platinum nanoparticles

Nanoparticles ranging from 2-12 nm was the first to be reported in platinum and was synthesized using >10% *Diopyros kaki* leaf extract as reducing agent from an aqueous H(2)PtCl(6).6H(2)O solution at a reaction temperature of 95°C⁵⁶. Platinum nanoparticles of 23 nm size have been prepared using leaf extract of *Ocimum sanctum* as reducing agent from aqueous chloroplatinic acid at a reaction temperature of 100°C that finds application in water electrolysis⁵⁷.

Zinc nanoparticles

To the best of our knowledge, biological approach using milky latex of *Calotropis procera* has been used for the first time as a reducing material as well as surface stabilizing agent for the synthesis of spherical-shaped ZnO-NPs. The structure, phase, and morphology of synthesized product were investigated by the standard characterization techniques. Milky latex of *Calotropis procera* has been used for the synthesis of spherical ZnO NP_S. Highly stable and spherical ZnO NPS have also been synthesized using *Aloe vera* extract⁵⁹.

Conclusion

The "green" route for nanoparticle synthesis is of great interest due to eco-friendliness, economic prospects, feasibility and wide range of applications in nanomedicine, catalysis medicine, nano-optoelectronics, etc. It is a new and emerging area of research in the scientific world, where day-by-day developments is noted in warranting a bright future for this field.

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