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Green Synthesis of Metal Nanoparticles

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Abstract:
In the last two decades, metal nanoparticles have been created much interest among the scientists due to its application in different field such as sustainable energy, food safety, environmental science, catalysis, medicine etc. The synthesis of the metal nanoparticles in the chemical method involves large energy consumption, environmental pollution which leads to health problems. The green synthesis of metal nanoparticles using plant extract as the reducing agent are more beneficial than the chemical methods due to low cost, environment friendly, health safety. In this review, green synthesis of Ag NP, Au NP, Pd, Pt NP and their applications are discussed.

Keywords: Green Synthesis, Biosynthesis, Metal Nanoparticles, Alloy Nanoparticles, Magnetic Nanoparticles

Introduction:
In recent years, application of nanoparticles in the different fields of science and technology is generating a huge interest among the scientists all over the world. Nowadays, the application of nanomaterials in medical field is an emerging area of research due to their small size, large surface area, solubility and also easy eco-friendly green synthesis from plant extracts. By definition, nanoparticles have the size in between individual molecules and their bulk counterparts i.e having nanoscopic dimension of range 1-100 nm.[1,2] Due to their large surface area, nanoparticles exhibit exclusive physicochemical properties and have immense application in medicine,[3] cosmetic,[4] food industry,[5] chemical industry,[6] drug delivery system, biosensors, bioimaging, cancer therapy etc.[7] Nanomaterials have the immense potential in the diagnosis as well as the treatment and prevention of COVID-19. To fight against this virus, development of nano-based infection-safe PPE and antiviral disinfectants and surface -coatings is necessary. Metallic nanoparticles, especially silver nanoparticles have potential antiviral, antifungal and antibacterial activity. The silver nanoparticles are now used to prepare disinfectants having self-sterilization property and self-cleaning system for surfaces. Use of metal nanoparticles, biogenic nanoparticles, polymeric nanoparticles, nanocomposites, photocatalytic nanostructured films in the disinfectants and sanitizers are reported to keep the surfaces of door handles, mobile, laptop keyboard etc clean for long time.[8]
So, the synthesis of nanoparticles especially metal nanoparticles is a challenging research area of chemistry in the recent past. Among the various methods, green synthesis of nanoparticles has gained a greater interest due to its simple, cost-effective and environment-friendly approach. So, we are interested to make a review on this topic.
Ag nanoparticles are found to be synthesised easily by using silver metal ion solution and a reducing biological agent. Ag nanoparticles are reported to be synthesised from different medicinal plants like *Oryza annum*, *Zea mays*, *Aloe vera* etc and also different parts of the different plants e.g leaf, seed.

Approaches involved in the green synthesis of nano particles:

Professor Norio Taniguchi (Tokyo Science University) defined the term 'nanotechnology' as follows: "Nanotechnology deals with the processing of separation, consolidation and deformation of materials by one atom or by one molecule".[9] The beginning of advanced nanotechnology was first revealed by Richard Feynman in 1959.[10] The field of nanotechnology has obtained vast motivation in electronics, chemical industry, food industry, biomedical applications, pharmaceutical industry, optics etc. This technology is also reliable for environmental challenges in various fields i.e. drug delivery, catalysis, waste water treatment, solar energy harvesting etc.

Nanometrial synthesis can be earned by either of two approaches.

Top-down approach: This approach involves the dissociation of bulk material to fine particles with the help of suitable lithographic techniques i.e. grinding, sputtering and milling.[11]

Bottom-up approach: In this appoarch, nanoparticles involve through self association of atoms into new nuclei.[12]

TYPES OF NANOPARTICLES:

Metallic nanoparticles

Metallic nanoparticles can be defined as nanometals in nanoscopic dimension (1-100 nm). In 1857, Faraday first introduced the existence of metallic nanoparticles in solution.[13]

Important characteristics of metallic nanopaticles are as follows,

A. Large surface area to volume ratio.
B. Large surface energy.
C. Specific electronic structure provides by their transition between molecular and metallic states.
D. Plasmon excitation.
E. Quantum confinement.

Different types of synthesised metallic nanoparticles are silver, gold, palladium, platinum, etc. Silver nanoparticles are reported to have antibacterial property and are also used in medicinal, textile, catalysis chemistry.

Magnetic nanoparticles

Magnetic nanoparticles formed by two types of components : magnetic component (Fe, Co, Ni) and chemical component.[14] The importance of this type of nanoparticles is due to its attractive properties. These nanoparticles are reported to be used as catalysis [15], medical diagnostics [16] and tissue- specific targeting.[17]

Metal oxide nanoparticles

Metal oxide nanoparticles are characterised by metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges. In solution it produced metal oxo or metal hydroxo polymers.[18]

Alloy nanoparticles

The synergestic effect of nanoalloys enhances the specific properties of alloys and thus these nanoparticles are reported to be applied in the field of electronics, engineering and catalysis.[19]

SYNTHETIC METHODS OF NANOPARTICLES:

Physical approach

In general methods in the physical approach to nanoparticles include electrospraying, evaporation-condensation, laser pyrolysis, high energy ball milling and laser ablation are discharge method, atomizati-

on, metal sputtering etc. are other physical approaches.

Advantages of physical nanoparticles

A. No solvent contamination in the prepared thin films and uniformed distribution of synthesised nanoparticle.[20]
B. This approach can be useful as a nanoparticle generator equipment.[21]
C. Laser ablation technique generates metal colloids without presence of chemical reagents in solution.[22]

Disadvantages of physical approches

A. Large space is required.
B. Large amount of heat generated.
C. Time consuming.

Chemical approach

In general methods in the chemical approach to nanoparticles include sol gel method, hydrothermal synthesis, the microemulsion technique, polyol synthesis etc.

In the synthesis of silver nanoparticles the common reducing agent is $NaBH_4$. In spite of this, gallic acid, sodium citrate, hydroquinone, elemental hydrogen are also used.

Advantage of chemical nanoparticles

Surfactants e.g. thiols, amines, acids and alcohols are generally used which protect the particles from sedimentation, agglomeration and loss of surface properties.

Disadvantages of chemical nanoparrticles

A. Solvents and chemicals used are toxic and hence harmful to both human and environment.
B. Byproducts generated are not ecofriendly.

Biological approach

In biological approaches, the synthesis of nanoparticles includes bacteria, fungi or plants. In most of the cases reducing agents are present in cells. There is not necessary to add capping and stabilizing agents from outside.

Advantage of biological nanoparticles

Due to the widely distribution of reducing agent in biological system there is no need to add reducing agent from outside.

IMPORTANCE OF GREEN SYNTHESIS:

Green synthesis is required to avoid the production of unwanted or harmful by-products through the build-up of reliable, sustainable, and eco-friendly synthesis procedures. The use of ideal solvent systems and natural resources is essential to achieve this goal. Some basic principles of "green synthesis" can thus be explained by several components like minimization of waste, reduction of pollution and the use of safer (non-toxic) solvent. Green synthesis of metallic nanoparticles has been adopted to accommodate various biological materials e.g., bacteria, fungi, algae etc.

PLANT EXTRACT IS MORE IMPORTANT THAN BIOSYNTHESIS:

Plant extract has several advantages since the use of microorganism required stringent control on cell culture.[23] By plant extract method, the synthesis of nanoparticle is the kinetics for this path is higher compared to other biological method. The important compounds in the plant extract are hydroxyl and carbonyl groups. Both functional groups allowed plant extract to act as reducing agent as well as

stabilizing agent. Various part of plants i.e. fruit, steam, root, leaf have been used for green synthesis of nanoparticles due to the classy phytochemicals.[24] The phytocompounds such as terpenoids, polyphenols, polyols are responsible for bioreduction of metallic ions which are obtain in plant extract.[25] The common method used to quantify the concentration of reducing agents in the extract is through Folin-Ciocalteu method.

SYNTHESIS OF NANOPARTICLES:

Ag nanoparticles

Ag nanoparticles are found to be synthesised easily by using silver metal ion solution and a reducing biological agent. Ag nanoparticles are reported to be synthesised from different medical plant like *Cinamomum cmphora*,[26] *Oryza sativa* , *Zea mays* etc. Silver ion's reduction is the easiest and cheap method for silver nanoparticles production. Modification of silver nanoparticles with the help of polymers and surfactants exposed high microbial activity Gram-negative and Gram-positive bacteria.[27]

Santoshkumar et.al. synthesised silver nanoparticles by the reduction of $AgNO_3$ solution with the *Nelumbo nucifera* plant extract. A brownish yellow color solution was designated as the formation of silver nanoparticles (AgNPs).

Philip et. al. prepared AgNPs from the leaf extract of *Hibiscus rosa sinensis*

Plant seed are also reported to be used to synthesise AgNPs. In 2009, Bar et.al. synthesised silver nanoparticles by adding the seed extract of *Jatropha curcas* to 10-3 M aqueous solution of $AgNO_3$ (20 ml). After heating the mixture at 80°C for 15 minute solution turned reddish indicating the synthesis of silver nanoparticles

Biosynthesis of silver nanoparticles is also done from the bark of certain plants. Kumar et. al. suggested that the bark extract may be the precursor of AgNPs. and Santhishkumar et. al. synthesised AgNPs from the bark extract of *Cinnamon zeylanicum* which was reported as the perfect source of silver nanoparticles with high antimicrobial activity.

Au Nanoparticles

Gold nanoparticles (AuNPs) have been widely employed in bionanotechnology based on their unique properties and multiple surface functionalities. The ease of AuNP functionalization provides a versatile platform for nano biological assemblies with oligonucleotides, antibodies and proteins. Bioconjugates of AuNPs have also become promising candidates in the design of novel biomaterials for the investigation of biological systems. The first study of gold nanoparticles was performed by Shankar and his group in 2003. This reaction proceeds through the using of terpenoids which was responsible for the reduction of gold ion to gold nanoparticles and the time required around 48h. Shankar et. al also reported that the synthesised nanoparticles were of various shapes such as spherical, decahedral, triangular and icosahedral.[28] The same group synthesised AuNPs from the neem extract. Chandran et.al. reported that the shape and size of gold nanoparticles depends upon the quantity of leaf extract used. Large sizes triangles of nanogold were formed by use of less amount of extract of $HAuCl_4$ solution, The morphological study revealed the formation of more spherical shaped nanoparticles when the quantity of leaf extract was increased..

Temperature plays an important role in formation of certain shape and size of the synthesised gold nanoparticles as reported by Song et al. in the biosynthesis of gold nanoparticles by *Diopyros kaki* and *Magnolia kobus* leaf extracts. They also suggested that at higher extract concentration and higher

temperature, nanoparticles produced were smaller in size and shape was found to spherical whereas in lower concentration and temparatureVarious morphologies were obtained.

Zhang and his coworkers used chloroplast of *Trifolium* leaves as a reductant and stabilizer. These nanoparticles showed high crystallinity having plane (111) as predominant orientation and spherical particles of size 20 nm in diameter. Toxicology assays against gastric mucous cell line GES-1 and gastric cancer cell line MGC-803 by using 3-(4,5-dimethylthia-zol-2-yl)-2,5diphenyltetrazolium bromide (MTT) method revealed the nontoxic nature of nanoparticles. SERS (sur-face-enhanced Raman spectroscopy) studies revealed the capability of gold nanoparticles could substantially enhance the Raman signals of rhodamine 6G without any treatment. Hence, these nanoparticles were biocompatible as well as having immense potential for hypersensitive detection of the biomarker in vivo and in vitro studies.[29]

Islam et al. reported that gold nanoparticles synthesised by leaf extract of *Salix alba* were suitable for numerous pharmaceutical and biomedical applications due to its excellent antifungal activity, antinociceptive and muscle relaxant properties. Gold nanoparticles were also synthesised recently from various plant extracts such as *Cofea Arabica*,[30] *Bacillus marisfavi*,[31] *Croton sparsiforus* leaves extract,[32] *Aeromonas hydrophila*.[33]

Pd and Pt Nanoparticles

Biogenic synthesis of palladium (Pd) and platinum (Pt) nanoparticles from plants and microbes has captured the attention of many researchers because it is economical, sustainable and eco-friendly. Plant and their parts are known to have various kinds of primary and secondary metabolites which reduce the metal salts to metal nanoparticles. Shape, size and stability of Pd and Pt nanoparticles are influenced by pH, temperature, incubation time and concentrations of plant extract and that of the metal salt. Both palladium and platinum are high-density silvery white precious metals. Biogenic fabrication of palladium and platinum nanoparticles using various plant species such as *Anogeissus latifolia, Cinnamom zeylanicum, Cinnamomum camphora, Curcuma longa, Doipyros kaki, Gardenia jasminoides, Glycine max, Musa paradisica* etc. have been reported.[34]

Palladium nanoparticles were also synthesised from protein-rich soybean leaf extract containing amino acids. Lebaschi et al. 2017 synthesised Pd nanoparticles by using renewable and nontoxic black tea leaves (*Camellia sinensis*) extract reducing and stabilizing agent. Lebaschi et al. 2017 also found that these nanoparticles were applicable in the reduction of 4-nitrophenol as well as in heterogeneous & effective catalysts in the **Suzuki coupling reaction** along with phenylboronic acid and aryl halides. The recycling capability of the catalyst was found 7 times without losing its catalytic activity,

For the reduction of Pt^{4+} into platinum nanoparticles (avg size 5-50nm), leaf extract of *Azadirachta indica* was used. Ahmed et al. reported that the protein was responsible to reduce the chloroplatinic ions into Pt nanoparticles. The terpenoids, amino acids, ascorbic

acid, certain proteins, and gallic acid present in tulsi leaf extract played an important role in the reduction of platinum ions. Some platinum nanoparticles were found to be the rich source of antioxidants and have brilliant antibacterial and antifungal properties as well as these are excellent for therapeutic purposes.[35]

Applications:

Nanoparticles are of great interest for their broad area of applications in industries,[36] biomedical fields,[37] electronics,[38] markets,[39] energy,[40] and especially in chemistry.[41] Biomedical applications of silver and gold nanoparticles show immense application in interdisciplinary field of

nanotechnology. The use of gold nanoparticles specifically in cancer therapy for the detection of cancer cells, protein assay, immunoassay, and capillary electrophoresis creates great interest in the synthesis of gold nanoparticles. Thes e are also reported to be used as biomarkers.

Silver nanoparticles have wide area of applications like biolabeling, sensors, antimicrobial activity, antibacterial activity, cell electrodes, integrated circuits, etc. Due to showing antimicrobial activity, these are applicable in numerous fields such as medicine, health, packaging, animal husbandry, various industries, military, cosmetics, and accessories.Palladium nanoparticles were derived by Hippophae rhamnoides Linn leaf extract have been studied in Suzuki–Miyaura coupling reaction for heterogeneous catalytic activity. In the Suzuki–Miyaura coupling reaction. Pd nanoparticles work as a catalyst. Some Pd nanoparticles revealed outstanding antioxidant properties at a lesser dose of nanoparticle, as well as these nanoparticles, worked as nanocatalyst for environmental remediation by showing catalytic activity in the reduction of dyes such as methyl orange, methylene blue, coomassie brilliant blue G-250, and reduction of 4-nitrophenol.[42] Platinum nanoparticles were used for evaluation of anticancer activities using four various cancer cells such as hepatocellular carcinoma (HePG-2), breast cells (MCF-7), and colon carcinoma cells (HCT-116).

Conclusion:

During the last some decades, increasing demand for green chemistry and nanotechnology pushes toward the adoption of green synthetic routes for the synthesis of nanomaterials via plants, microorganisms, and others. Green synthesis of nanoparticles has been the area of focused research by researchers in the last years by adopting an eco-friendly approach. Much research has been carried out on the plant extract-mediated nanoparticles synthesis and their potential applications in various fields due to their cost-effectiveness, nontoxic route, easy availability, and environment-friendly nature. Moreover, they have a wide area of applications such as catalysis, medicine, water treatment, dye degradation, textile engineering, bioengineering sciences, sensors, imaging, biotechnology, electronics, optics, and other biomedical fields. Additionally, plants contain some unique compounds which help in synthesis as well as increases the rate of synthesis. The use of plants for green synthesis of nanoparticles is an exciting and developing part of nanotechnology and has a noteworthy effect on the environment toward sustainability and further development in the field of nanoscience. The future expectations from the green route of nanoparticles synthesis are that the applications of these will grow exponentially, but there is a need to concern about the long-term effects of these on animal and human being as well as accumulation of these in the environment is a subject of worry which has to be resolved in future. These biogenic nanoparticles can be used in nanoweapons against phytopathogens as well as in the disinfection of water in various forms for environmental remediation. In the drug delivery system, these nanoparticles might be the future thrust for the biomedical field.

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