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Green synthesis, characterization and applications of metal nanoparticles

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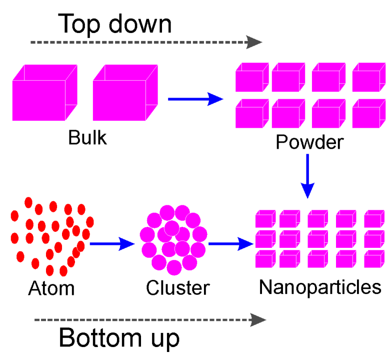
Abstract

Nanotechnology is the most promising area of research for its wide range of applications. It deals with the creation and control of particles having size 1-100 nm at least one of their dimensions. Metal nano particles are important component of nanoscience. Various methods have been developed and modified for the synthesis of metal nanoparticles. Among the several methods biogenic reduction of metal salts to corresponding metal nano particle is a green method due to low cost, absence of hazardous chemicals, without drastic condition, very mild and eco-friendly reaction condition. In this review, bio based synthesis and applications of silver, gold and palladium nanoparticles have been discussed.



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1 Introduction

Nanotechnology has gained the importance in the forefront of research over the past few decades for its wide applications in diversified fields like electronic storage system, biotechnology, targeted drug delivery etc. and the key element of nanotechnology is nanoparticles. By convention particles with size range 1 to 100 nm in at least one of their dimension are called nanoparticles. Nanoparticles shows unique properties compared to their respective particles at higher scale due to high surface area to volume ratio. As the nanoparticles hold such unique properties, they are suitable candidate in biomedical applications because several biological processes occur in nano scales.[1] Nanoparticles are different types from various aspects. Depending upon dimension they are zero dimensions such as nano dots, one dimension such as grapheme, two dimensions such as carbon nano tube and three dimensions like gold nanoparticle. Again depending upon their shape and size they are called cylindrical, tubular, spherical etc. The revolution of nano concept occurs a long back at 1959 by Nobel laureate physicist Richard P. Feynman., one of his famous lecture entitled “There is Plenty of Room at the Bottom” where he proposed the possibility of nanolevel formation by accumulation of atoms or scaling down of bulk. [2]

Metal nanoparticles are highly interested in recent years for their unique optical, catalytic, electronic as well as physical properties and due to presence of these properties they have potential applications in different areas like optical, electronic, catalytic, magnetic materials and in medicine.[3] A significant attention has been devoted for the last two decades to synthesize size controlled and stabilized metal nanoparticles.[4] A number of different physical [5] as well as chemical methods such as mechanical grinding,[6] laser irradiation,[7] electrochemical reduction,[8] photochemical reduction[9] and heat evaporation [10] have been used for the synthesis of MNPs. Synthesis of MNPs by these physio-chemical methods releases hazardous substances increases the pollution of earth atmosphere. Even, MNPs synthesized under drastic conditions and stabilized with toxic chemicals limit their use in many of its applications especially in medicine and biodiagnostics. Hence it is the time that requires the advancement in the synthesis process of MNPs for a sustainable development. Therefore, the green synthesis of MNPs involving reduction of metal salts to metal utilizing the natural product extract is the best alternative process among the several reported methods. Advantageous of this method over the traditional synthetic methods is that stabilizing or capping agents not to be needed because the phytochemicals from natural extract can play the role of both reducing as well as stabilizing agents.

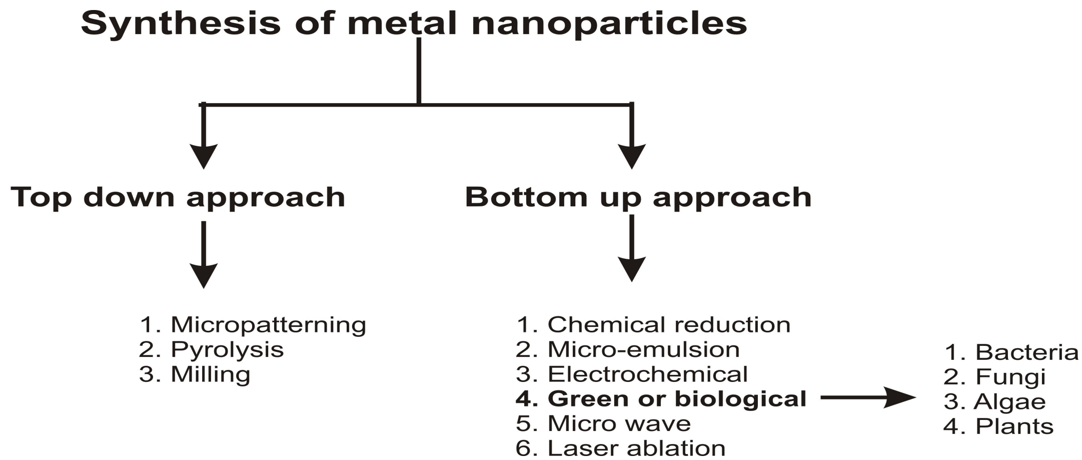

Fig. 1: Generalized flow chart of various physico– chemical approaches of nanoparticles synthesis with highlighting of biological synthesis.

This biological process is a bottom up approach of synthesis of MNPs and more favorable than other physical as well as chemical processes because in this process no toxic chemicals and drastic conditions required. The extract of natural products like different parts of plants, microbes can reduce metal ions and stabilize the MNPs. This process is cost effective, eco-friendly, sustainable and generates MNPs without contamination.[11,12,13, 14] The biological process also can recover expensive metals from wastes. [15] The bio-molecules like polyphenols, proteins, carbohydrates are responsible for the formation of MNPs and due to attachment of such biological molecules with MNPs can improve their antimicrobial activity.[16, 17] Among several nanoparticles silver, gold and palladium nanoparticles utilizing this method are drawn much more interest due to attractive physiochemicals properties and large reactive surfaces of nanoparticles as well as the method is easy, low cost and sustainable.

2 Green syntheses of metal nanoparticles

During the last decade the researchers not only attempt to synthesize new nanomaterials but also gave their attention towards synthetic procedures by which at low cost, eco-friendly without utilizing toxic chemicals MNPs should be prepared. The developed procedures of synthesis of MNPs are categorised as mainly two types (Fig.1), one is “Top down” where a bulk material is sequential break down until the desired nano size formed and other is “Bottom up” where the atomic levels are successively build up to fabricate nano dimension.[18] Although ‘Top- down’ approaches is a prosperous method leading bulk scale production of MNPs but use of high energy, impure material, particles with wide range of size and lack of stability are the major disadvantages whereas ‘bottom up’ approach is most promising technique to get nano materials with less defects. The several processes commonly used in bottom up approaches are sol-gel, spinning, laser pyrolysis, chemical precipitation, chemical vapour deposition and biosynthesis etc. The biosynthesis method is eco-friendly and synthesis of MNPs are required non toxic and biodegradable components so it also known as green synthesis. In spite of several methods this is most important (fig.1). In this method micro-organisms have been utilized to fabricate MNPs without hazards chemicals and drastic reaction condition as well as absence of any stabilizing or capping agents. A plausible mechanism for synthesis of MNPs also proposed (Fig.2).

2.1 Silver nanoparticles

Spherical shaped silver nanoparticles (AgNPs) with size 4-15 nm were synthesized using leaf extract of *Paederia fotedia* L. The synthesized AgNPs shows significant antibacterial activity against both gram classes’ of bacteria.[19]The leaf extracts of *Syngonium podophyllum* was utilized for the synthesis of spherical shaped AgNPs with average size 40 nm. These synthesized nanoparticles show efficient antifungal activity against *C. albicans.*[20] Behravan et.al synthesized AgNPs using leaf and root extract of Berberis vulgaris. The synthesized particles were spherical and 30 to 70 nm size range. Authors also carried out antibacterial activity of AgNPs on Escherichia colia and Staphy-lococcus aureus bacteria.[21] Bar et.al have reported the latex of *Jatropha curcas* was utilized for synthesis of AgNPS. They also demonstrate that particles were 10 to 20 nm size and stabilized by cyclic peptides.[22] The leaf extracts of *Moringa oleifera* used to synthesize AgNPs by Jerushka S Moodley et.al. They synthesize AgNPs using both fresh and freeze dried leaves and in both cases produced AgNPs of average size 9 and 11nm respectively. These nanoparticles exhibit antimicrobial activity against bacteria and fungai.[23] Pragyan Roy et. al have synthesized AgNPs using leaf extract of *Azadirachta indica* .These particles also show antimicrobial activity on microbes.[24] Silver nanoparticles also synthesized from leaf extract of *Ocimum sanctum*. These nanoparticles exhibit antibacterial and antifungal activities.[25]

2.2 Gold nanoparticles

Madhuri Sharon et. al have reported the synthesis of AuNPs with 25-30 nm size utilizing extract of *Chlorella pyrenoidusa* at 100^{o}C. They also show that shapes of generated AuNPs depend upon the pH of reaction medium. At alkaline pH the particles were spherical where as at acidic medium produces anisotropic nanostructures. The synthesized AuNPs were.[26] The bark extract of *Terminalia arjuna* have been used to synthesize AuNPs[27]. The particles were different shaped like spherical, triangular and FCC crystalline. The authors also demonstrate the excellent neuroprotective potential of synthesized AuNPs towards cholinesterase inhibitory and antiamyloidogenic activity and proposed that these can be utitilized for designing drugs for treatment of Alzheimer'sdisease. Roshanak Khandanlou et.al used leaf extract of Backhousia citriodora to synthesize AuNPs with average size 8.4 nm. The synthesized AuNPs showed a significant dose dependent anticancer activity on the MCF-7 breast cancer cell line and theHepG2 liver cancer cell line.[28] Punuri et al. have reported synthesis of AuNPs utilizing ethanolic leaf extract of Piper betle. Synthesis of AuNPs with different morphology and size 10 to 35 nm was completed within 18 seconds. They also demonstrate the cycotoxic activity of AuNPs on MCF-7 and HeLa cancer cell lines.[29] The extract of Punica granatum was utilized to synthesize AuNPs at room temperature and very mild reaction condition. The size of the synthesize AuNPs were varied with concentration of extract. These AuNPs can be used as catalyst for the sodium borohydride reduction of 4-nitro phenol.[30] Leaf extract of Acacia nilotica can generate stable AuNPs in water medium within few minutes without heating. The synthesized AuNPs were 6 to 12 nm size depending upon concentration of leaf extract and can act as excellent catalyst for reduction of nitro phenol to amino phenol.[31] The extract of *Nerium oleander* steam bark utilized for the synthesis of biocompatible AuNPs . The synthesized AuNPs were mostly spherical along with other shaped having size range 20-40 nm. But higher concentration of bark extract flower like particles composed of smaller particles produced. These particles show excellent antioxidant, anticancer and catalytic activity.[32]

2.3 Palladium nanoparticles

PdNPs have been prepared from xanthum gum in autoclave at 15 psi pressure and 120°C for 10 min. The prepared particles were mostly spherical with average diameter 10 nm. These nanoparticles can act as excellent catalyst for sodium borohydride reduction of 4-nitro phenol.[33]The leaf extract of *Chrysophyllum cainito* have been used to synthesize PdNPs. Synthesis of PdNPs have been completed within 2-3 hours at RT but on heating it formed almost instantly. The synthesized particles utilized as excellent catalyst for C-C coupling reactions and reduction reations.[34] Mohammed Rafi Shaik et. al have reported the synthesis of PdNPs using aqueous extract of aerial parts of *Origanum vulgare* L. Synthesis was carried out by heating the mixture of plant extract and palladium chloride with stirring at 90°C for 2 hour. These PdNPs used as recyclable catalyst for selective oxidation of alcohols.[35] PdNPs have been prepared from fruit extract of *Terminalia bellirica*. The synthesized particles were triangular with size range from 30 to 45 nm and show the anti fungal activity against A*spergillus niger*.[36] *The aqueous leaf extractof GarciniapedunculataRoxb* was utilized to synthesize PdNPs in presence of starch as bio-stabilizer. The synthesize particles act as excellent catalyst towards Suzuki cross coupling reaction and selective oxidation of alcohols. These also shows antimicrobial and anti-biofilm activities to *Cronobactersakazakii* strain AMD04.[37].

3 Characterization metal nanoparticles

Different microscopic and spectroscopic techniques were utilized to characterize the metal nanoparticles. Spectroscopic techniques were UV-Vis spectroscopy, fourier transform infrared spectroscopy (FTIR), energy disperse x-ray spectroscopy (EDX). The microscopic techniques are optical microscopy (OM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Other techniques also used to characterize nanoparticles were selected area electron diffraction (SAED), X-ray diffraction (XRD), and dynamic light scattering (DLS) study etc.

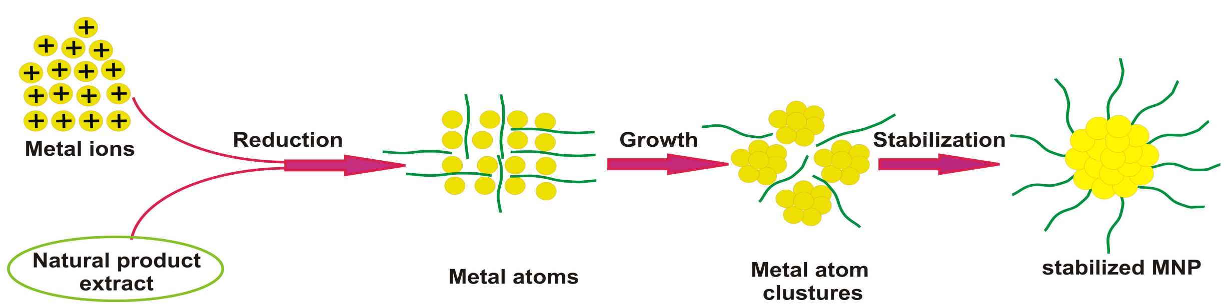

Fig. 2: Mechanism of formation of metal nano particles.

4 Conclusion

Synthesis of MNPs using natural product extract has gain significant attention in recent years because it is a greener method. This process is biocompatible and eco-friendly due to use of non toxic natural products, mild reaction condition and also cost effective. Due to absence of hazardous chemicals and drastic reaction condition the synthesized particles are more pure and stable than other conventional methods, so that they have potential applications in catalysis, cancer therapy, drug delivery, medicine, biotechnology, electronics etc.

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