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Green Synthesis of Bimetallic Nanoparticles and its Applications: A Review

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Abstract

Nanotechnology has been the topic of concern from past few decades and recent advances have made it far more interesting. Usage of nanoparticles in various technological applications make them "tiny heroes" that carry out certain processes which were otherwise impossible. In this review we discuss about metal nanoparticles and their forms such as bimetallic nanoparticles. Metal nanoparticles can be classified based on their origin, dimension as well as structure and their synthesis process can be physical, chemical as well as greener route i.e. biological. Bimetallic nanoparticles are of more interest than metal nanoparticles as they show better optical, electrical and medical applications due to their peculiar mixing patterns and synergistic effects of two metal nanoparticles that form bimetallic. Their synthesis from plants and microbes is a topic of talk because it's environmentally benign, less expensive and less time consuming. Application of bimetallic nanoparticles as catalysts is most promising one due to large surface area and small size, but bimetallic nanoparticles as biosensors, antimicrobials, in ground water remediation and for drug delivery has given good results.

Keywords: Nanotechnology, Nanoparticles, Bimetallic Nanoparticles, Greener Route

INTRODUCTION

Nanoscience and Nanotechnology studies has been transpired from previous years in a wide range of artifacts realm. This technology gives scope for the development in many fields including medicine, where conventional methods show several limitations [1]. Nanotechnology speaks to the plan, creation and use of materials at atomic, molecular and macromolecular level, keeping in mind the end goal to deliver new nano-sized materials [2]. As of late, the meeting of nanometer size scale advancements and biological techniques has paved way for the new field of Nanobiotechnology. It is generally centered around the creation, control, and utilization of materials at the nanometer scale for cutting edge biotechnology [3]. The expression "nano" originates from the Greek word "nanos" which means dwarf and signifies an estimation on one-billionth (10^{9}) of a meter in size. It envelops frameworks whose size is above sub-atomic measurements and beneath naturally visible ones (i.e. > 1 nm and < 100 nm) [4].

Types of Nanoparticles:

Nanoparticles are of several types and can be classified on the basis of:

1. Origin,
2. Dimension, and
3. Structural organization

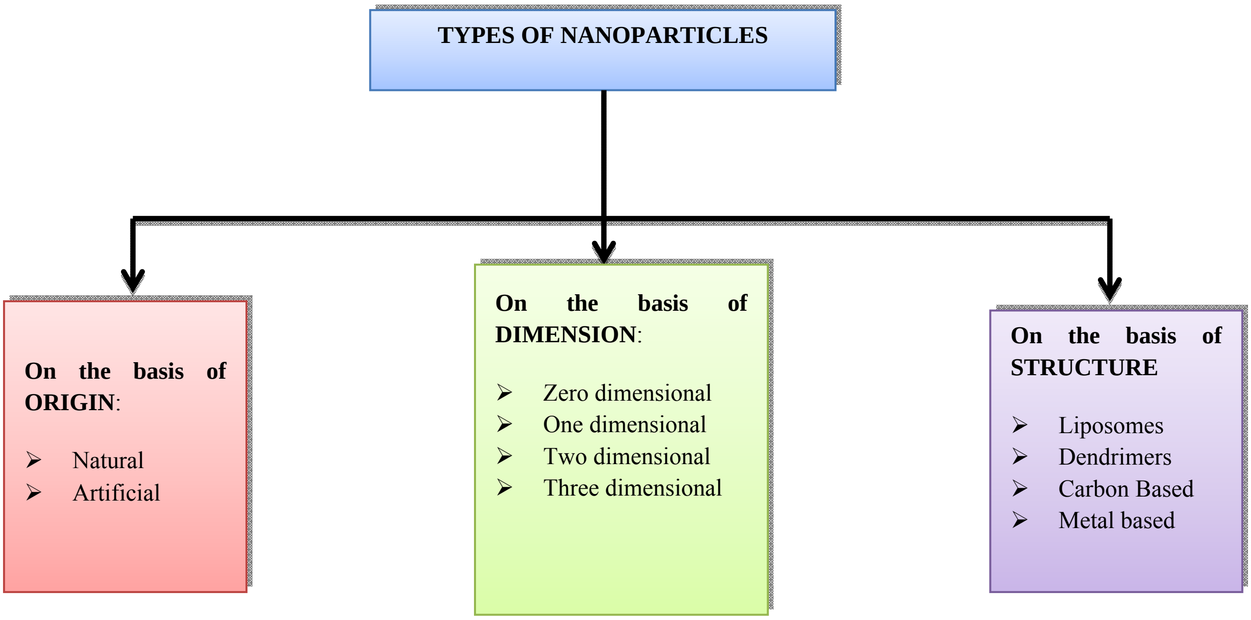

Figure 1: Flowchart representing Types of Nanoparticles

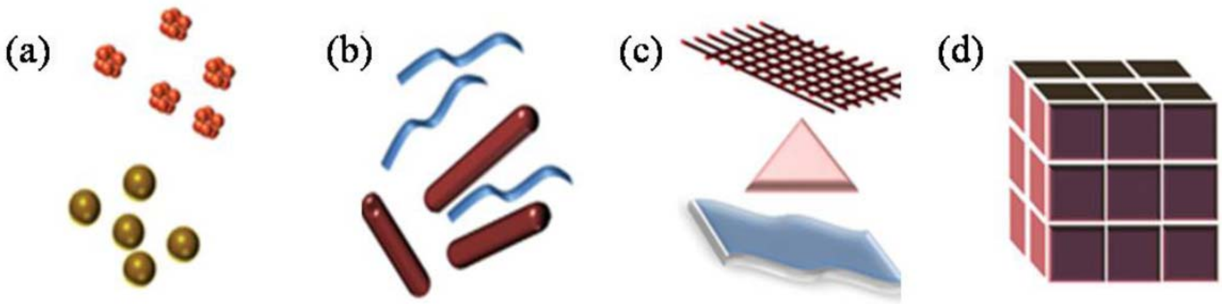

Figure 2: (a) 0-D spheres and clusters, (b) 1-D nanofibers, wires, and rods, (c) 2-D films, plates, and networks, (d) 3D nanoparticles [https://nccr.iitm.ac.in/2011.pdf]

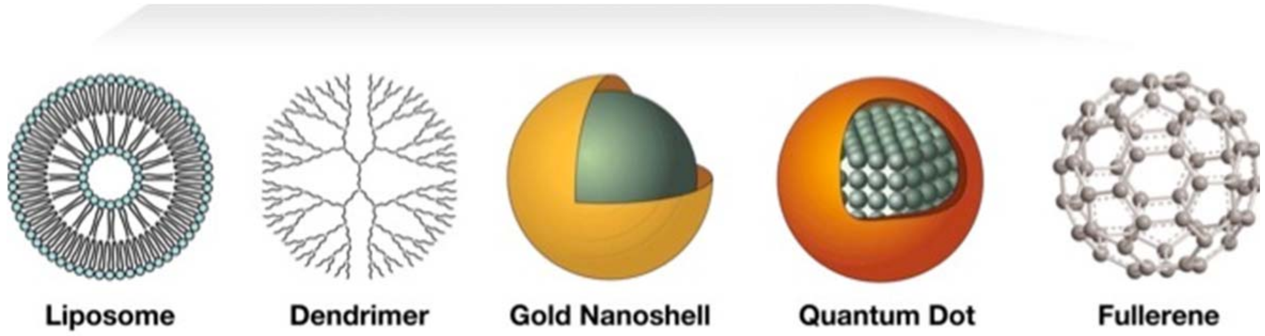

Figure 3: Different nanoparticles based on structural configuration [15]

On the basis of Origin, natural nanoparticles are nanoparticles that belong to natural resources are called natural nanoparticles such as virus, protein, antibodies etc. Artificial nanoparticles are those nanoparticles that are intentionally prepared for a purpose following proper manufacturing process and required techniques are called artificial nanoparticles such as carbon nanotubes, metal nanoparticles, nanomembranes etc.

On the basis of Dimension [5-7], zero dimensional (0-D) are those nanoparticles that hold critical range of 1-100 nm in all three directions of space vectors are zero dimensional nanoparticles. Quantum dots and metal nanoparticles are perfect examples of zero dimensional nanoparticles. Most of these particles are spherical in shape or may be cubic, polygonal or clusters. As name suggests in one dimensional (1-D), one dimension of the nanostructure is outside the nanometer range and two spatial vectors are committed to critical length scale thereby allowing growth only in third direction. Example: Nanowires, nanorods etc. These nanomaterials are usually long but with small diameter. Two dimensional (2-D) nanoparticles have two dimensions of the nanostructure outside the nanometer range and only one vector is committed to critical length scale hence allowing growth in two spatial directions. Example: Nanofilms, nanosheets, nanowalls etc. The surface of these films can be of several micrometer square but thickness would be in nano range only. Three dimensional (3D) nanoparticles have all three dimensions are outside nanoscale range. These include bulk materials like fullerene.

On the basis of Structural Configuration [8], there are liposomes that are bi-layered concentric vesicles composed of natural or synthetic phospholipids. Liposomes can alter the pharmacokinetic profile of drug loaded [9]. Dendrimers are polymers with nano dimensions and controlled structure. Dendrimers are widely used for targeted drug delivery [10]. Carbon based have hollow cage-like architecture, include carbon nanotubes and fullerene. Small dimensions of carbon nanotubes along with excellent electrical, mechanical and physical properties make them very unique [11]. Fullerenes resemble certain bioactive molecules with similar dimensions and therefore have potential applications in medicines [12]. Metal based, as the name suggest, have metal as component of these particles. They can be in the form of nanoshells or closely packed semiconductors like quantum dots [13]. Depending on the number of constituent particles metal nanoparticles can be classified as bimetallic (composed of two metals), trimetallic (containing three metals), or multimetallic (containing more than three metals) [14].

Present review focuses on bimetallic nanoparticles. Bimetallic nanoparticles are synthesized by a combination of two metal nanoparticles with several architectures [16].

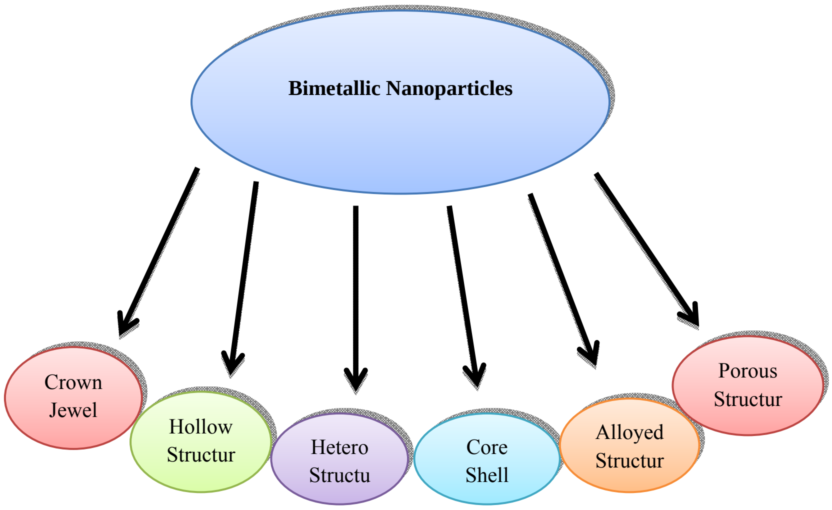

Figure 4: Schematics of Bimetallic Nanoparticle Types

a) Crown Jewel Structure – In this type of architecture, one metal atom (jewel atom) is mustered on the surface of other metal in controlled manner. The 'jewel' metal is usually a costly one with catalytic properties, e.g.: Au, Ag, Pt
b) Hollow Structure – Possess large pore volume and high surface to volume ratio. Hold utility in nanoreactor.
c) Hetero Structure – One metal forms branches over the nanocrystalline form of other.
d) Core Shell Structure -It's a simple arrangement where active metal shell is supported on another metal present as a core. Core shell bimetallic nanoparticles are emerging as propitious catalysts with good efficiency [17].
e) Alloyed Structure – Bimetallic alloys are formed when two different metal atoms possess homogenous distribution in a single particle.
f) Porous Structure – These are bimetallic alloys with increased surface area, low density and high gas permeability, thereby proving to be better catalysts than their solid counterparts.

ADVANTAGES OF BIMETALLIC NANOPARTICLES OVER MONOMETALLIC NANOPARTICLES:

Bimetallic nanoparticles (BMNPs) have characteristic mixing patterns and geometrical architecture which enhances their functionality [18,19]. They show better stability, selectivity and catalytic activity over monometallic nanoparticles [20-24]. BMNPs as catalysts can carry out certain chemical conversions that were unexampled with monometallic nanoparticles as catalyst. This is because bimetallic nanoparticles have a certain combination of two metals wherein each performs a particular function to carry out the overall reaction mechanism [25,26]. The synergistic effects of two metal nanoparticles show certain surprising new properties which increases their function and application in many different fields [27,28]. By merely changing the individual components as well as geometrical architectures, physical and chemical properties of BMNPs can be modified in order to make them perform better [29,30]. Alloyed nanoparticles show better physical and structural properties as compared to their bulk samples such as enhanced solid solubility with decreasing particle size [31]. BMNPs have outshined monometallic nanoparticles due to their better and improved electronic, optical and catalytic performances [32,33].

Nanoparticle synthesis involves two major approaches:
I. TOP DOWN APPROACH
II. BOTTOM UP APPROACH

Top down synthesis is cutting of bulk material to get nano-sized particles, where as in bottom up synthesis atoms build up into new molecules which grow into clusters and then form particles of nano-scale [34]. Since two techniques hold significant differences, therefore below we discuss a few of them.

Table1: Differences between Top-Down and Bottom-Up approaches of Nanoparticle Synthesis [35,36]

Top-Down Approach	**Bottom-Up Approach**
Starts with bulk solid materials	Starts with atoms, ions and molecules
Fragmentation of bulk materials into nanoscale particles in presence or absence of catalyst by application of external mechanical force	Atoms, ions and molecules act as building blocks which assemble into nanoscale clusters with atomic or molecular precision
No specific control over shape and size	Specific control over shape and size
Faster than bottom-up	Comparatively slow
For large scale industrial productions	For laboratory purposes
Processes involved are: Ball milling, melt mixing, mechanical grinding etc.	Processes involved in bottom-up approaches are chemical precipitation, sol-gel process, pyrolysis.

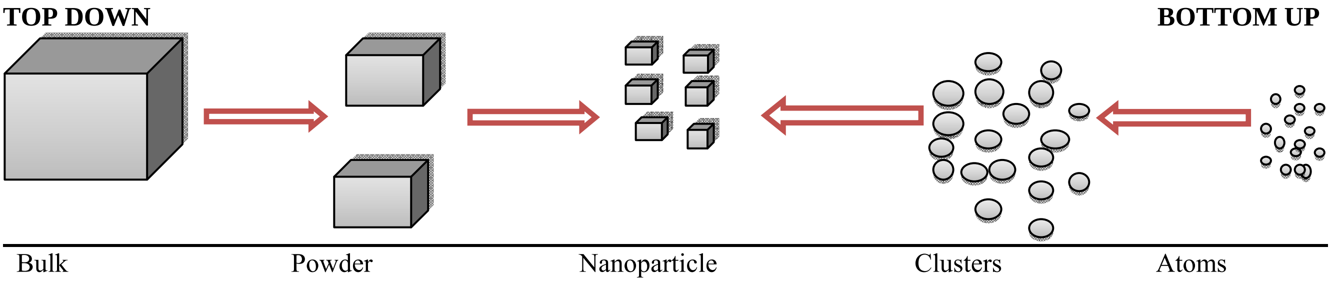

Figure 5: Schematic representation of the building up of Nanoparticles

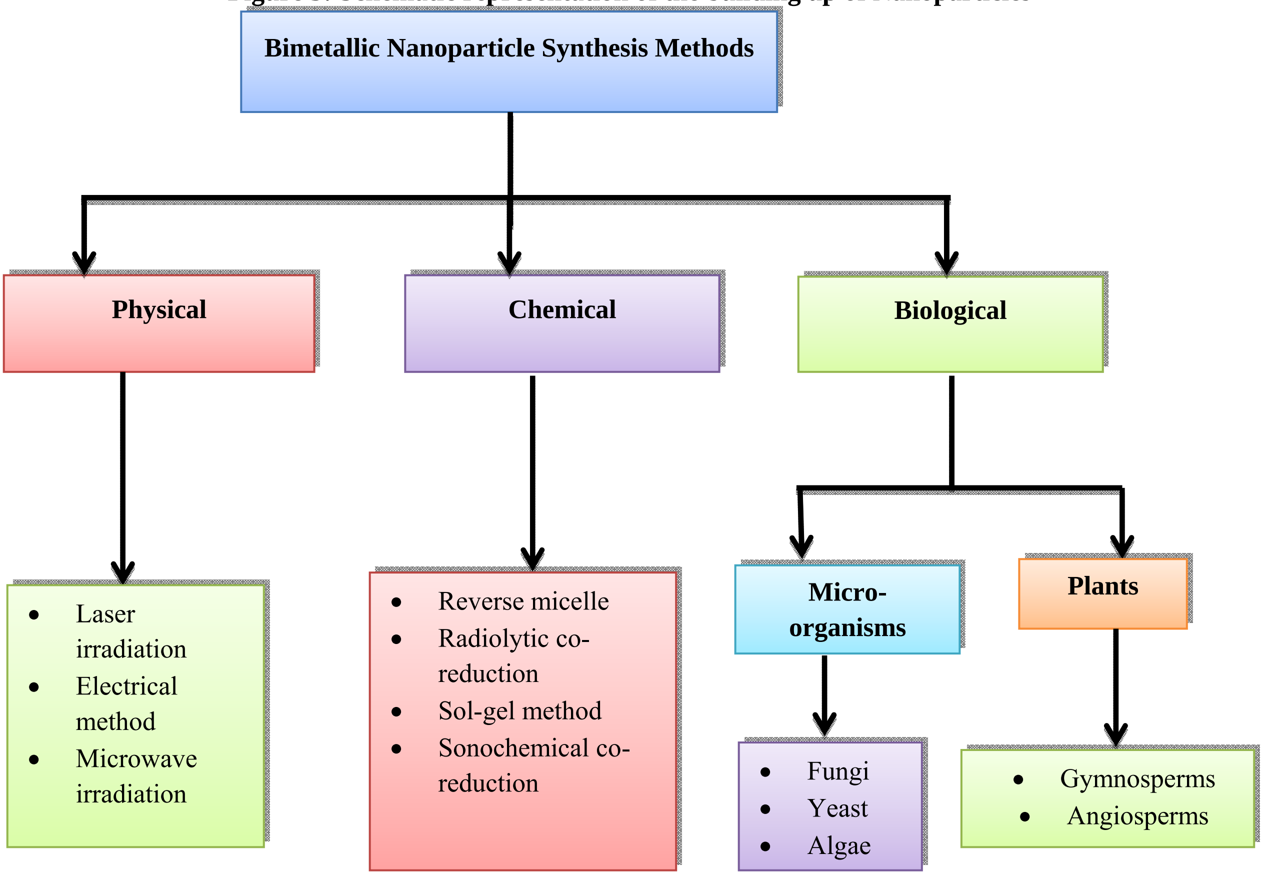

Figure 6: Flowchart representation of Synthesis methods of Bimetallic Nanoparticles

Synthesis methods of metal nanoparticles can be:

- Physical
- Chemical
- Biological

Physical Methods- These methods holds certain advantages over chemical methods such as, no solvent contamination in prepared film and uniformity in nanoparticle formation. Several physical methods for synthesis of nanoparticles can be:

Laser Irradiation Method- Bimetallic nanoparticles can be synthesized without using any chemical agent and only by laser irradiation of high intensity on aqueous solution. For Example, Pt-Au bimetallic nanoparticles, Pt and Au are photosensitive therefore in dark room Pt-Au precursors are prepared by dissolving chloroauric (III) acid tetrahydrate and chloroplatinic (IV) acid hexahydrate in deionized water using concentration of 1.0×10−2 wt. % irradiating it with laser [38].

Electrical Method- In this process an electrode gap is created by automatic control system and procedure is done at this electrode gap and constant current. Particles synthesized are kept in cooling liquid under the effect of gravitational force [39]. For Example: Cu-Ag bimetallic nanoparticles, helps in production of water dispersible copper and copper-silver nanoparticles at room temperature, requires inert atmosphere. Results were investigated using various spectroscopy techniques like XRD, UV-Visible and TEM [40].

Microwave Irradiation- Microwave heating replaces use of chemicals and reduces reaction time, therefore preferred for bimetallic synthesis. For Example, Fe-Ru bimetallic nanoparticles, ruthenium (III) chloride hydrate ($RuCl_3 \cdot H_2O$) and iron (III) chloride hexahydrate

($FeCl_3 \cdot 6H_2O$) were used to prepare aqueous solution by adding above two in 1, 2- propanediol. 0.1M ammonia is added drop wise with continuous stirring. Resulting solution irradiated using microwave heating giving dark brown colloidal solution of Fe-Ru bimetallic nanoparticles. Colloidal dispersion is then precipitated by acetone to remove chloride ions and then dried in vacuum to be redispersed in mixture of ethanol and water before characterization [41].

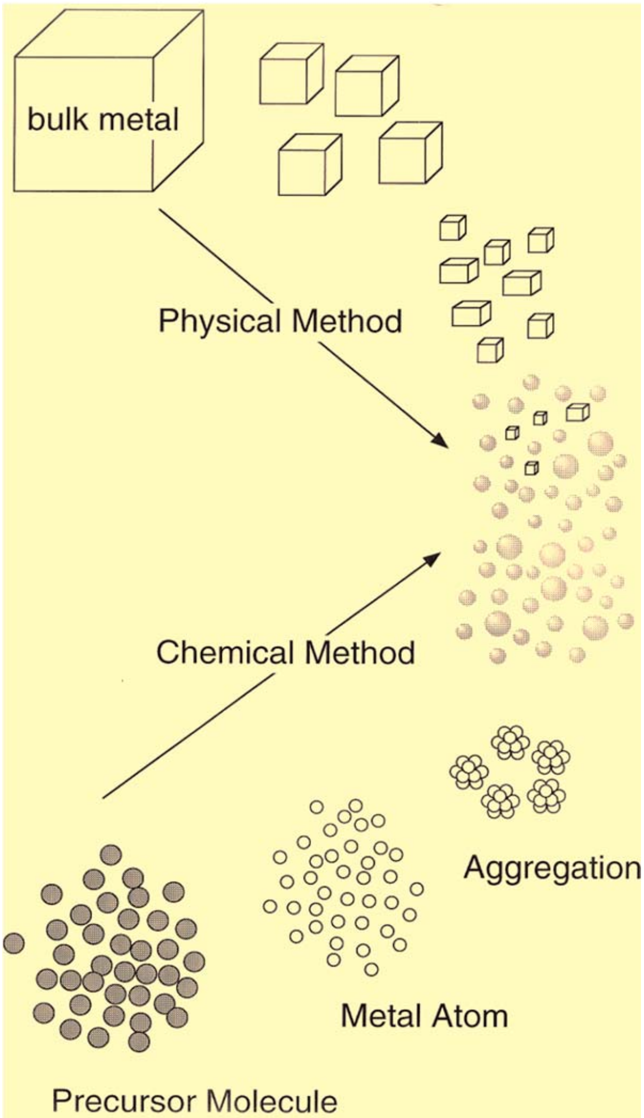

Figure 7: Schematic Illustration of Preparative Methods of Nanoparticles [37]

Chemical Methods- Advantages of chemical methods over physical methods are that the techniques are not complicated, economic, diverse sizes and shapes can be synthesized, large quantities can be obtained in short span of time, doping of foreign atoms during synthesis is possible. Various synthesis methods via chemical route are:
Reverse Micelle Method- Reverse micelles are found in water in oil micro-emulsions with certain composition as nano-sized droplets. These days they are extensively used in synthesis of many nano sized particles [42]. For Example, synthesis of Fe-Co bimetallic nanoparticles, wherein, calcium carbonate is supported by Fe-Co. Carbon nanotubes were prepared by using 5% Fe-Co/$CaCO_3$ by chemical vapor deposition. Reverse micelle technique enable precise control over size of carbon nanotubes [43].
Radiolytic Co-Reduction Method- this method produces highly dispersed as well as uniform sized metal clusters [44]. Nanoparticles can be synthesized with the use of ionization radiations such as UV, X-Ray as well as Gamma Radiation in presence of stabilizer only and no other chemicals are required [45-47]. Example, Ag-Pd bimetallic nanoparticle synthesis carried out by co-reduction of silver nitrate ($AgNO_3$) and ammonium hexachloropalladate (IV) in aqueous solution with Triton-X 100. Characterization done by XRD, TEM and SAED. Ag-Pd bimetallic nanoalloy showed better electro-catalytic activity than Ag nanoparticles [48].

Sol-Gel Method- Here monomers are converted into colloidal suspension i.e. sol which act as precursor of either integrated network i.e. gel or discrete particles. Process occurs in four steps, they are, hydrolysis, condensation, growth and lastly agglomeration of particles [49]. For Example, synthesis of Cu-Ce oxides, where stoichiometric amounts of Ce (III) and Cu (II) nitrates in presence of urea in aqueous solution was used in synthesis of Cu-Ce oxide solutions kept with continuous stirring at 80 ^oC until gel is formed and then kept for cooling. Gel is then decomposed by raising temperature to 250 ^oC to form precursor $CeCu_2O_4$ which is then calcinated at 600 and 900 ^oC respectively [50].
Sonochemical Co-Reduction- This method help in synthesizing nanoparticles of large surface area and small size as compared to other methods [51]._Example of this method is synthesis of Au-Ru bimetallic nanoparticles. Here Au (III) and Ru (III) ions are sonochemically co-reduced in aqueous solutions using polyethylene glycol as stabilizer. Characterization of synthesized bimetallic nanoparticles is carried out by XRD, UV, IR, SEM and TEM [52].
Biological Methods-Several Advantages of biological methods over chemical and physical methods are that the processes are environment friendly, less time taking**,** almost negligible industrial waste, no use of toxic chemicals, uses inherent biological methods for nanoparticle fabrication, its safe and hold various applications that are not possible with physical or chemical synthesis methodologies.
Synthesis of nanoparticles via physical and chemical routes is expensive, hazardous and time consuming. Therefore, there is more focus on nanoparticle synthesis using natural resources such as plants and microbes which is termed as ‘green synthesis’ [53,54]. Plant mediated synthesis of nanoparticles is better than microbes mediated as the process doesn’t include any synthetic protocols and toxic chemicals as well as has high reaction rate since need to grow microbes is eliminated [55,56]. Biosynthesis of Au-Ag bimetallic alloys from fungal biomass and from single cell protein *Spirulina plantesis* was reported [57,58].

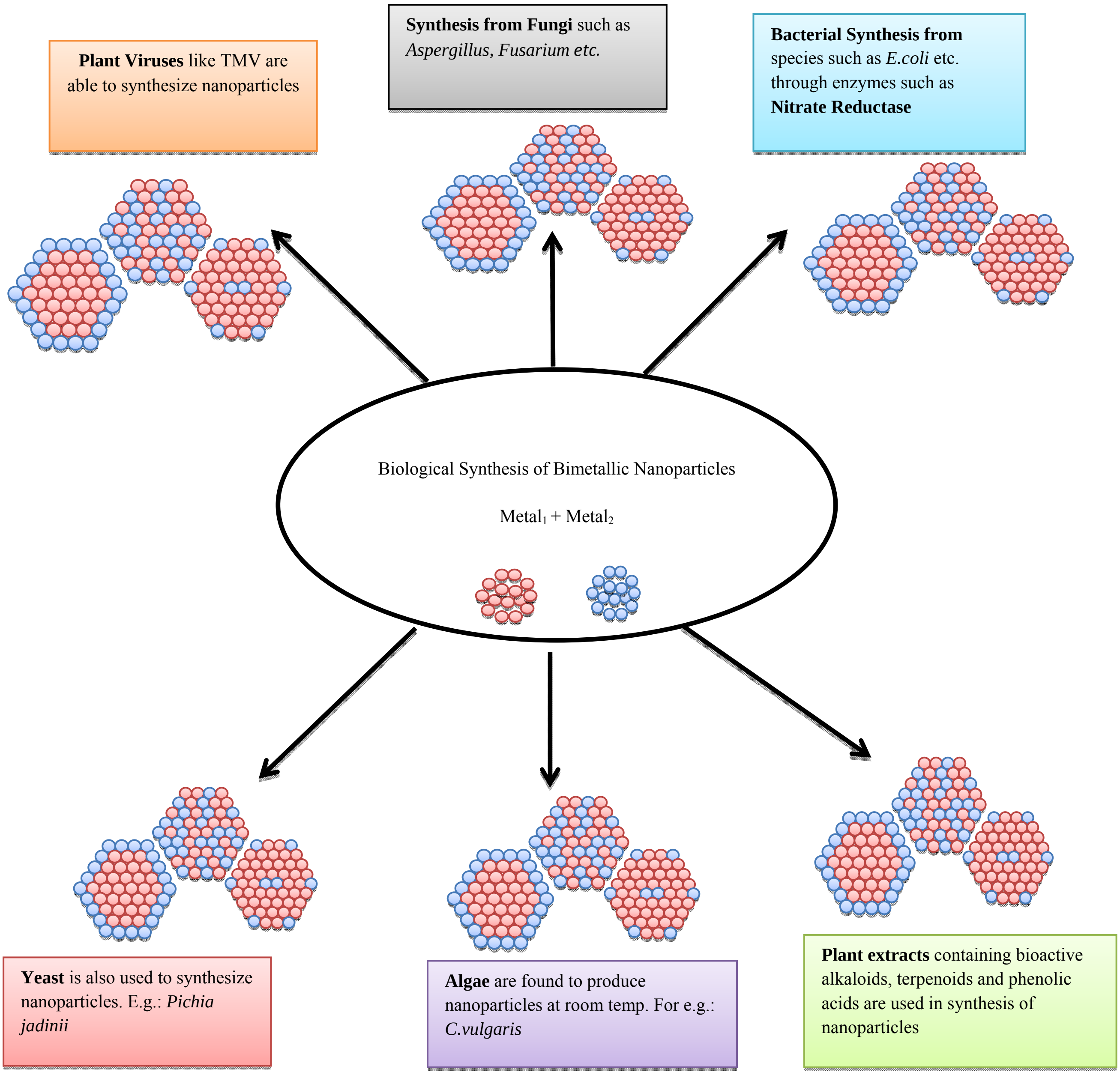

Figure 8: Schematic representation of Biological Synthesis of Bimetallic Nanoparticles with different architectures i.e. Core-shell, Alloy, and Crown-Jewel

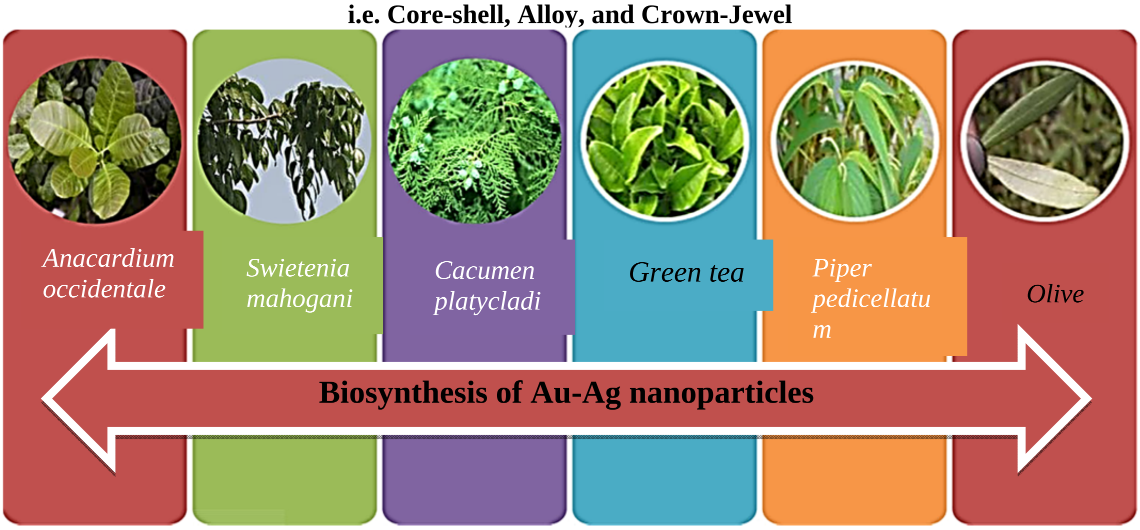

Figure 9: Various natural biosources for the preparation of Au-Ag nanoparticles [62]

Few other examples are also discussed below.

Biosynthesis of Au-Ag bimetallic nanoparticles:

I. Using Persimmon (*Diopyros kaki*) leaf extract- During exposure to Persimmon leaf extract there was competitive reduction between Au^{3+} and Ag^{+}, which lead to the formation of 50-500 nm cubic Au-Ag bimetallic nanoparticles which were later characterized by UV, EDS, SEM etc. [59].
II. Using aqueous extract of Mahogany (*Swietenia mahogani* JACQ.) leaves- Silver nitrate ($AgNO_3$) and Chloroauric Acid ($HAuCl_4$) were used as source of Ag^{+} and Au^{3+} respectively, which when exposed to Mahogany leaves extract, that contain polyhydroxy limonoids, undergoes reduction to give stabilized bimetallic Au-Ag alloy nanoparticles. Techniques used for their characterization were UV-Visible spectroscopy and TEM [60].
III. Using Piper pedicellatum C.DC leaf extract- The chemical constituents i.e. catechin, gallic acid, courmaric acid and protocatechuic acid present in leaf extract of P.pedicillatum C.DC leaf extract act as reducing, stabilizing and capping agents respectively which cause reduction of Au (III) and Ag (I) ions and results in formation of fcc Au-Ag bimetallic nanoparticles, which were characterized by FTIR, XRD, TEM etc. [61].

Biosynthesis of Ti-Ni bimetallic nanoparticles: Nanoparticles of Ti-Ni were produced by bio-reduction technology where pH was the controlling parameter of the medium in which they were grown. Characterization of structure and morphology was done using high-angle annular dark field in electron microscopy as well as HREM. The nanoparticles were found to be fcc core-shell type with Ni as shell. Dimensions were in range of 1-4 nm [63].

Biosynthesis of Fe-Pd bimetallic nanoparticles: Green tea (*Camellia sinensis*) extracts contain many polyphenols which can act as reducing, chelating and capping agents for synthesis of nanoparticles. Membranes containing reactive nanoparticles were immobilized on PVDF membrane. Reactivity of nanoparticles in membrane was observed even after three months of repeated usage [64].

Biosynthesis of Au-Pd bimetallic nanoparticles: In presence of Cacumen Platycladi leaf extracts in aqueous medium there is simultaneous bio reduction of Au^{3+} and Pd^{2+} which result in formation of Au-Pd bimetallic nanoparticles of ~7nm. Characterization techniques used were UV, XRD, and FTIR etc. [65].

APPLICATIONS OF BIMETALLIC NANOPARTICLES

Bimetallic nanoparticles hold numerous applications including electrical, optical, catalytic and biomedical. Bimetallic nanoparticles serve as very good catalysts. Reduction reaction between Mohr's salt and [Co $(NH_3)_5$Br] $(NO_3)_2$] can be effectively catalyzed by Au-Ag nanoparticles which is basically due to transfer of charge from Ag ions to Au ions [66]. Another example is Pt-Ru bimetallic nanoparticles that act as anode catalyst for methanol oxidation done at low temperature in methanol fuel cells [67]. Reduction reaction of aromatic nitro compounds by sodium borohydride is catalyzed by Pt-Ni bimetallic nanoparticles [68]. CO oxidation, result in 100% conversion of CO at room temperature. The reaction was catalyzed by Ni-Pt bimetallic hollow spheres [69]. Bimetallic nanoparticles have promising usage in field of nanomedicine. Tunable chitosan-capped spiky urchin like Au-Ag bimetallics created via single reactor synthesis process, when targeted against cancer in photothermal cancer therapy gave promising results in ablating cancer cells. Ag-Se bimetallic nanoparticles synthesized using gallic acid and quercitin as standard phenolics and flavonoids have seen to be toxic against cancer cells and therefore can be used in preventing or at least lowering oxidative stress related to degenerative diseases [70]. Bimetallics can be effectively used in drug delivery as they have high surface area to volume ratio, hence can cross blood-brain barrier and epithelial cell junction to reach target site [71]. These bimetallic nanoparticles, due to their excellent electrical and optical properties can be used as biosensors. Platinum based bimetallics such as Pt-Co, Pt-Ni and Pt-Fe have very good catalytic activity and thus can amplify the detection limits of biosensors [72]. Bimetallic nanoparticles are of great importance in restitution of environment. Their role in decontamination of ground water has given significant results. Fe-Cu bimetallic nanoparticles can be used in clearing nitrates in groundwater via in-situ remediation [73]. Pd-Au bimetallic nanoparticles exhibit great deactivation resistance and hydrodechlorination for removal of chlorinated ethenes from ground water [74]. Nanofluids can enhance thermal conductivity when suspended in heat-transfer liquid. Ag-Au bimetallic nanoparticles in nanofluids perform the job with promising results [75]. Nanoparticles can be used as electrodes for electrical conductivity i.e. Au-Ag alloys has high performance as an electrode due to decreased inertness [76]. Bimetallics are excellent for electroplating and fabrication. Alloys of Au with Ag, Pt, and Pd have shown promising results in Microelectromechanical systems (MEMS) switch fabrication. They can also be used in surface enhanced spectroscopy as substrates for providing large electromagnetic enhancements [77]. Bimetallic nanoparticles also serve as great antimicrobials. Bimetallic nanoparticles as antimicrobials can complement the role of antibiotics in combating with bacteria. These nanoparticles can interfere with bacterial growth either by disrupting their membrane or by producing ROS (reactive oxygen species) that cause destruction of DNA and also impede its protein functioning machinery [78].

Ag-Au bimetallics synthesized from *Gracilaria sp*. show antibacterial activity against *Staphylococcus aureus* and *Klebsiella* [79]. Also, Au-Ag bimetallic nanoparticles synthesized from *Oscimum basilicum* (Basil) flower and leaf extracts have antibacterial activity against *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Bacillus subtilis, Escherichia coli* etc. [80]. Ag-Cu bimetallic nanoparticles prove to be promising anti-microbials against gram positive bacteria-*Bacillus subtilis*. Therefore their synergistic effects with antibiotics and sulfa drugs can be exploited for preparation of medicines against bacteria [81]. Ag doped ZnO nanoparticles show anti-bacterial activity against *Staphylococcus aureus* and *Bascillus subtilis* by altering MIC (Minimum Inhibition concentration) especially in case of *S.aureus* [82]. Cu-Ni bimetallic nanoparticles have shown bacteriostatic effect against certain bacterial strains like *Escherichia coli*, *Staphylococcus aureus*, *Staphylococcus mutans* [83]. Fe-Ag magnetic bimetallic nanoparticles show very good anti-fungal and anti-bacterial effect against a number of pathogenic micro-organisms. These bimetallic nanoparticles showing antibacterial activity can be used in the field of nanomedicine, to form nanodrugs against human pathogens in order to fill the gaps wherein antibiotics fail to give positive results.

CONCLUSION

This review is written to get an insight about bimetallic nanoparticles, their synthesis methods and their possible applications. Bimetallic nanoparticles are combination of two metal nanoparticles which are fabricated by a number of synthesis methods which include physical, chemical as well as biological processes. Greener routes are preferred because they are environmentally salubrious and safe. Need to synthesize them is their advantages over monometallic nanoparticles. Synergistic effects of two metals in bimetallics carry out certain functions which were otherwise not possible with monometallic nanoparticles alone. Bimetallic nanoparticles are of great interest as they hold a number of applications in the field of nanomedicine, for drug delivery, as catalysts, as anti-microbials, in bio-sensing, in overcoming environmental pollution and several others which are a topic of further study. Development of improved bimetallic nanoparticles will surely prove to be a boon to a society.

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