

SUSTAINABLE SYNTHESIS OF BIMETALLIC NANOPARTICLES USING PLANT SOURCES: A SHORT REVIEW

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Abstract: Activity of transition metal salts can be significantly enhanced when they are transformed into their nano range. The magical properties of nanoparticles are due to their extremely small particle size (1-100 nm), greater surface area, and many more important physicochemical properties. Due to the possibility of synergistic interactions, recently bimetallic nanoparticles (BMNPs) gained more practical utility and popularity as compared to their monometallic counterparts. Due to the high demand for bimetallic nanocomposites, the developments of their efficient and sustainable synthetic methods are becoming an important area of research in the present time. In this context, plant-based sources may serve as an innovative natural feedstock for assisting the synthesis of nanoparticles due to their outstanding reducing as well as stabilizing capacities. In this review, we are reporting the practical utilities of different plant sources and their extracts in designing the green synthesis of bimetallic nanocomposites (**Figure 1**). In addition to the green synthetic developments of BMNPs, some of their recent practical applications have also been highlighted in the manuscript, which may help researchers to find some innovative practical solutions for many challenging day-to-day issues.

Keywords: Plant sources, Green synthesis, Bimetallic nano particles, Applications

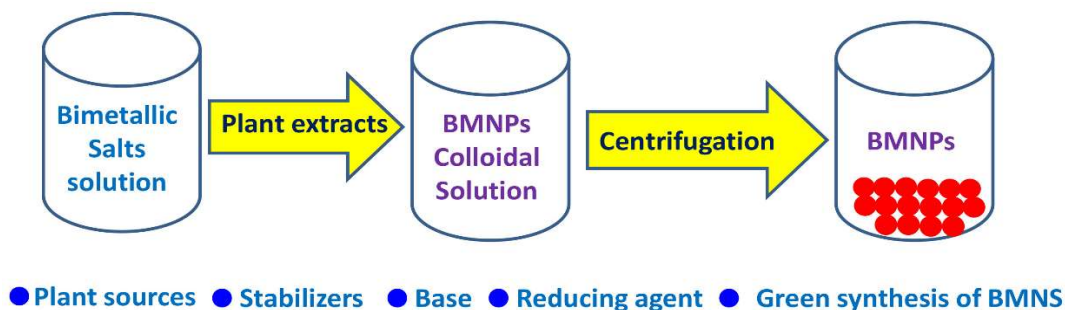


Figure 1: Green synthesis of bimetallic nano particles

1. Introduction:

Nanoparticles (NPs) are the very minute particles having sizes between 1 and 100 nm that appear at the atomic or molecular dimension to offer superior properties over their bulk counterpart. Due to their extremely small particle size, greater surface area, and fascinating properties, metal nanoparticles find special interest in the area of both the academic and industrial sectors [1-2]. When particles are designed to be in the nano range, their properties, like their thermal, optical, electrical, and mechanical nature, change magically [3]. Nanoparticles also provide important contributions in the material science division, which include the fields of electronics, semiconductors, optics, solenoids, lithium-ion batteries, smart windows, and paints [4]. In addition to these, nanoparticles are widely used in organic synthesis, water purification, and photocatalytic water-splitting experiments [5, 7].

Bimetallic Nanoparticles (BMNPs), are formed by the combination of two different metals. Bimetallic nanoparticles have attracted considerable attention as compared to monometallic nanoparticles in the scientific community because they can offer better properties due to synergistic interactions. These bimetallic nanoparticles can be categorized as multi-shell, core-shell segregated, intermetallic (alloyed), or heterogeneous, depending on the structural characteristics derived from the synthesis technique [6]. The process of bimetalization can significantly enhance the catalytic activity of the resulting nanohybrids, which may not be possible to achieve with monometallic nanoparticles. Additionally, alloying of two metals can lead to drastic structural changes to enhance their stability, conductivity and other physico-chemical properties [7]. In biomedical fields, alloyed nanostructures are widely utilized for their superior localized surface plasmon resonance (LSPR) effect and superparamagnetic properties, essential for biosensing and targeted drug delivery. Furthermore, in mechanical and electrical applications, the synergistic effects of bimetallic interfaces enhance heat conductivity and charge transfer efficiency, hence enhancing the performance of next-generation micro-devices [6]. Bimetallic nanoparticles are often synthesized using the co-precipitation or co-reduction of two metal precursors, employing stabilization techniques that rely on steric hindrance or electrostatic repulsion to inhibit aggregation. Various methods like sol-gel, co-precipitation, microemulsion, electrospray, laser ablation, and hydrothermal reaction are already employed for the synthesis of nanomaterials [8], but in most of the processes either the by-products are hazardous or the processes are difficult to perform and may require special precautions [9-10]. In this regard, the development of simple, cost-effective methodology and green techniques has always had an additional advantage over the others. Recently, the synthesis of NPs using reagents such as sugars, vitamins, biodegradable polymers, and special microorganisms such as *Escherichia coli*, *Streptococcus mutans*, and *Bacillus subtilis* as reductants, capping agents, or stabilizers has gained significant attention in nanotechnology [2]. However, cheap and naturally occurring sources such as plant-based material or extract may be one of the best choices compared to others, as they are ideal for large-scale biosynthesis of nanoparticles. In this context, synthesis of metal nanoparticles has been achieved using various parts of plants, such as leaves, roots, latex, seeds, stems, etc. [11]. Since uses of plant extract for synthesis of monometallic nanoparticles have been well explored by various scientists across the world, therefore, the same kinds of plant extract could also be used for the synthesis of bimetallic and polymetallic nanocomposites, which can offer multidimensional properties as compared to monometallic counterpart. This review mainly focuses on the green synthesis of bimetallic nanoparticles and their practical applications for maintaining environmental sustainability.

2. Synthesis of Bimetallic Nanoparticles:

In general, two methods such as “Top-Down” and “Bottom-Up” approaches are used for the construction of nanoparticles. Top-down synthesis requires the reduction of bulk materials to produce nanosized particles, whereas bottom-up synthesis involves the accumulating of atoms into new molecules that subsequently aggregate into clusters, finally resulting in nanoparticles (Figure 1) [12]. The first approach is typically attained through physical methods, and the second by biological and chemical methods.

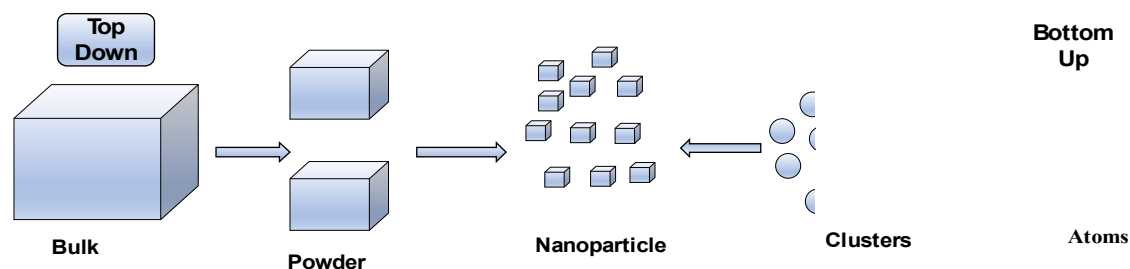


Figure 2: Schematic illustration of the formation of nanoparticles

Bimetallic nanoparticles can be synthesized in the solid, vapor, or solution phase. Under appropriate reaction conditions, bimetallic nanoparticles could be produced using metallurgical techniques that melt two kinds of bulk metals under proper heating conditions. [13]. However, it is very challenging to obtain nanocrystalline bimetallic compounds *via* solid-phase synthesis with high surface areas and most cases require high temperature followed by annealing for a long time. [14].

On the other hand, solution-phase synthesis is more powerful and versatile, as both the particle size and surface area of the nanoparticles can be tuned. By controlling the reaction parameters, including the concentration of

reactants, pH, the mole ratio between precursors and stabilizers, the reaction temperature and time, monodisperse bimetallic nanomaterials with unique shape or morphology could be achieved. [15].

Synthesis of bimetallic nanoparticles is generally achieved via two different procedures. One method proceeds through seed-mediated reduction followed by insitu generation of BMNs while the other can synthesize bimetallic nanoparticles by simultaneous reduction and stabilization. The rate of nanoparticle synthesis and their size, shape, and structure depend on the reducing agent used and other reaction conditions applied. Due to high demand for the advancement of sustainable routes for the synthesis of bimetallic nanoparticles, simple, cost-effective, eco-friendly, and efficient approaches are being envisaged currently [16].

Some of the reported methods for synthesizing bimetallic nanoparticles have been highlighted below: -

- I. **Photochemical and thermal and decomposition:** The isolation of the nanocrystal phase from the reactive phase becomes very difficult at high temperature, which is the main disadvantage of this process due to the involvement of pyrolysis of precursors in boiling solvents at high temperature. Due to the high energy requirement of the bond breakage, the thermal method is endothermic in nature. The isolation and study of nanomaterials having unusual size and composition is facilitated by the photochemical method [17].
- II. **Chemical Reduction:** Chemical reduction can produce metal nanoparticles in their zero-oxidation state. This approach involves two successive processes such as reduction and interaction between metallic and polymeric substances. Sodium borohydride, elemental hydrogen, Tollen's reagent, and ascorbic acid etc. are often employed as reducing agents for nanoparticle synthesis. This method is applied to the synthesis of core-shell structured bimetallic nanoparticles, and is known as one of the most promising approaches. The successive approach entails the reduction of one metal through the reduction of its salt, thereafter depositing it onto the core shell of another metal at the nanoscale. [17].
- III. **Hydrothermal approach:** Hydrothermal synthesis is the most commonly used tactic used for the synthesis of bimetallic nanoparticles. It is basically a solution-based approach. Under the influence of high temperatures (about 470°C) and pressures below 300 MPa, nanoparticles are produced. Here the dilution of components is allowed, which are normally non-soluble under normal conditions. The pH, temperature, and pressure of the medium are noted. This method is advantageous because it can produce a high yield of the bimetallic nanoparticles with excellent reproducibility. It also produces crystals of high quality and offers the ability to control the physical and chemical properties of the resulting nanoparticles. The high equipment cost and not being able to monitor the growth process of crystal are the disadvantages of this method. By this method, zeolites and nanoparticles of lead telluride have been synthesized [17].
- IV. **Green synthesis of bimetallic nanoparticles:** Green synthesis methods offer numerous advantages over chemical and physical methods, such as environmental sustainability, reduced time requirements, negligible industrial waste, reduced use of toxic chemicals, employment of natural biological processes for nanoparticle synthesis, enhanced safety, and a variety of applications that are not achievable through conventional synthesis methods. Consequently, there has been increased focus on nanoparticle synthesis by employing natural feedstock, especially plant extracts, which eliminates hazardous chemicals and promotes a rapid reaction time. The synthesis of metal nanoparticles has been achieved employing several plant components, such as roots, leaves, seeds, latex, and stems. The prevalent global study on plant extracts for nanoparticle synthesis suggests that similar extracts may simplify the synthesis of bimetallic and polymetallic nanocomposites, possibly providing enhanced characteristics relative to monometallic nanoparticles. [18].

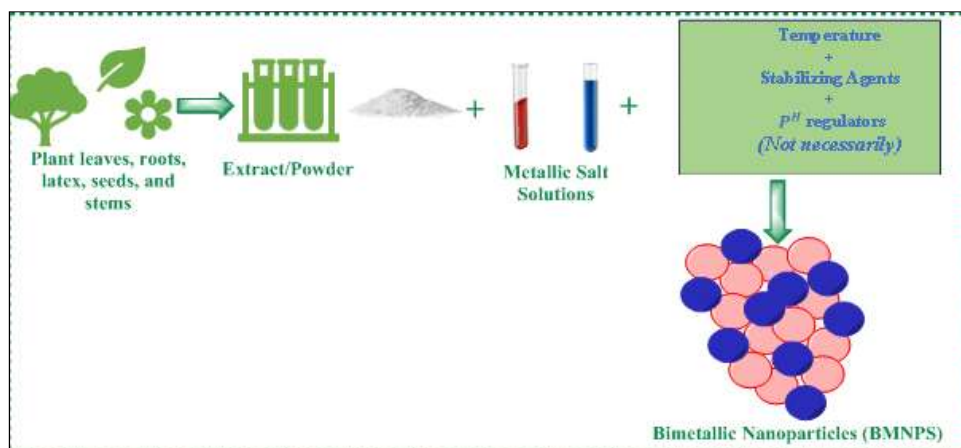


Figure 3: Green Synthesis of Bimetallic nanoparticles

A range of plant and fruit peel extracts were successfully employed as reducing or stabilizing agents for the synthesis of bimetallic nanoparticles, as detailed in the **Table 1**. This table also provides a systematic study of the different types of plant extract used during the synthesis of nanoparticles and gives information about the sizes of the bimetallic nanoparticles produced using the green approaches.

Table 1: An overview of the various plant sources used for the green synthesis of bimetallic nanoparticles

S No	Types of BMNPs	Plant source	Particle Size (nm)	References
1	Fe-Pd	Green tea (<i>Camellia sinensis</i>) extracts	20-30	[12]
2	Au-Pd	<i>Cacumen Platycladi</i> leaf extracts	7	[12]
3	Fe-Ag	<i>Salvia officinalis</i> leaves	48	[18]
4	Fe-Pd	Eucalyptus leaves	30-60	[18]
5	Cu-Pt	<i>Agrimoniae herba</i> plant extract	30	[18]
6	Pd-Ag	Stevia extract	5-15	[18]
7	Ag-Ni	<i>Salvadora persica</i> plant extract	24	[19]
8	Fe-Cu	<i>Fiscus</i> leaf extract	32-59	[20]
9	Ag-Au	Waste tea extract	50-80	[21]
10	Ag-Cu	Palmyra fruit pulp	300	[22]
11	Au-Ag	<i>Commelina nudiflora</i> aqueous extract	20-80	[23]
12	Ag-Cu	<i>Opuntia ficus-indica</i> plant extract	10-20	[24]
13	Ni-Bi	Aqueous toddy of <i>Borassus flabellifer</i>	100	[25]
14	Ag-Au	Keiapple fruit extract	10-60	[26]
15	Au-Pd	Flower extract of <i>Lantanacamara</i>	20-50	[27]
16	Au-Pt	<i>Crotoncaudatus</i> Geisel leaf extract	10-30	[28]
17	Cu-Ag	Extracts from the date palm tree	26	[29]

3. Applications of Bimetallic Nanoparticles:

Bimetallic nanoparticles (BMNPs) consisting of two transition metals are now becoming promising candidates for a wide range of applications. The most important advantages of BMNPs are their synergistic interactions, tuned catalytic properties, enhanced optical-electronic properties, outstanding stabilities, etc. Depending on the targeted applications, specific nanostructures having unique size, shape, or morphology are obtained *via* proper controlling of reaction conditions. This shape selectivity not only enhances the efficiency of the nanocomposite but also plays a major role in some important selective transformations.

Some important practical applications of BMNPs are being addressed in this present manuscript.

- I. **Biomedical:** Bimetallic nanoparticles find significant importance in drug discovery, targeted drug delivery, treatment of cancers *via* photothermal therapy, bioimaging purposes using magnetic nanoparticles as contrasting agents, repairing of bone and teeth, tissue and genetic engineering, treatment of microbial infections, antioxidant and anti-inflammatory agents, biosensors, immunity boosters, additives for reducing toxicity of exposed drugs, etc. [18,30-31]
- II. **Electronics:** Bimetallic nanoparticles provide significant contributions in the area of electronics. Due to their smaller particle size, greater surface area, and higher conductivity, they are found to be very useful candidates for the construction of supercapacitors, advanced memory chip devices, improved display screen devices, the reduction of power consumption in electronic devices, and the minimization of the size of transistors used in integrated circuits. [32-34]
- III. **Environmental remediation *via* photocatalysis:** Due to synergic effects of bimetallic nano particles, they offer narrow band gap, superior semiconducting behaviour, exceptional stability, smooth charge separation, minimized charge recombination possibility and hence provide valuable contributions in the area of photocatalytic degradation of harmful pollutants. [35-40]. Important photocatalytic applications of bimetallic nano particles include dye degradation, water purification, antibiotic degradation, pesticide degradation and conversion of toxic pollutants to harmless byproducts.
- IV. **Agricultural Science:** Bimetallic nanoparticles are found to be very effective in providing nutrients to soil, which has a direct effect on enhancing plant growth and large-scale production of crops. For example, bimetallic nanoparticles comprising Cu-Fe can serve as excellent nutrients that can enhance plant growth; bimetallic nanoparticles consisting of Ag-Fe or Mn-Fe can act as nano fertilizers; and bimetallic nanoparticles having Ag-Au, Ag-Cu, or Ag-Zn combinations offer biocide properties due to their potential antibacterial and antimicrobial properties. [41-43]
- V. **Application of bimetallic nanoparticles in catalysis:** Bimetallic nanocomposites, due to their synergistic properties, can play a significant role during homogeneous and heterogeneous dual catalysis. Some important catalytic applications include the use of Pd-Cu and Pd-Au hybrid systems for promoting efficient cross-coupling reactions, reduction reactions, and C-H activation reactions. [44]

4. Conclusion:

This review describes the various techniques used during the synthesis of bimetallic nanoparticles. The importance and advantages of green synthesis of bimetallic nanoparticles have also been highlighted. Conventional chemical approaches are expensive, require toxic reagents, and may require extra precautions for synthesizing bimetallic nanoparticles. On the contrary, the green synthesis of bimetallic nanoparticles is simple, cost-effective, and highly productive for the construction of bimetallic nanoparticles under environmentally friendly conditions. In summary, this review presents a systematic and concise study for synthesizing various bimetallic nanocomposites under sustainable conditions using some selective plant-based sources. The eco-friendly approaches described in this manuscript align with the principles of green and sustainable chemistry. In addition to the green synthesis of bimetallic nanoparticles, this review also highlights some important practical applications of bimetallic nanoparticles, such as in the areas of environmental remediation, removal or detoxification of harmful pollutants, photocatalysis, biomedical science, agriculture industry, etc. Even though bimetallic nanoparticles have wide ranges of applications in different areas of science, their catalytic uses in organic synthesis have not been explored well to date. The review also suggests the need for the development of bimetallic nanohybrids as catalysts, which could serve an important role in some vital heterogeneous catalysis and can promote sustainable organic synthesis.

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Conflict of Interests

The authors declare no conflict of interest.

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