

Review

Synthesis of Bimetallic Nanoparticles and Applications—An Updated Review

Dahir Sagir Idris  and Arpita Roy * 

Department of Biotechnology, Sharda School of Engineering & Technology, Sharda University,
Greater Noida 201310, India

* Correspondence: arbt2014@gmail.com or arpita.roy@sharda.ac.in

Abstract: The manipulation of matter at the atomic level (nanotechnology) has experienced an explosion in research interest in recent years. Bimetallic nanoparticles are vital due to their high biocompatibility, stability and comparatively less toxicity. The synthesis methods that include physical, chemical and biological methods are explored and explained in detail, along with their advantages. They have a wide range of applications due to their synergistic properties including biological applications (in medicine and agriculture), environmental application (in water treatment and removal of toxic contaminants), engineering application (in nanosensors, nanochips and nano-semiconductors) and chemical and physical application (in optics, catalysis and paints). The green synthesis approach is a promising method of synthesis that can give rise to more biocompatible and less toxic bimetallic nanoparticles due to increasing environmental pollution. However, despite these interesting attributes of bimetallic nanoparticle, there is still much work to be done to improve the biocompatibility of bimetallic nanoparticles because of their toxicity and potentially hazardous effects.

Keywords: nanotechnology; bimetallic nanoparticles; synthesis; applications



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1. Introduction

As the name implies, nanotechnology is a technology that deals with matter at the nanoscale level. It refers to the branch of science and engineering that deals with the manipulating of atoms or molecules at the nanoscale to design systems and produce devices for various applications. The main building block of nanotechnology is the nanoparticles. These nanoparticles are tiny in size, have a high surface area and exhibit a property known as quantum effects, which means irregular or unpredictable behavior [1]. Nanoparticles are of different types, and they can be classified based on structure (metal base, carbon base, dendrimers or liposome), dimension (zero, one, two or three dimensions) or origin (natural or artificial) [2]. Among the various types of nanoparticles, metal-based nanoparticles, especially those of noble metals, have more advantages than other nanoparticles. This is because metal-based nanoparticles are highly stable, biocompatible and possibly capable of large-scale production for biomedical and environmental applications [3]. However, despite having these fascinating abilities and properties, the application of metal based nanoparticles still needs to be improved in some fields of study due to their toxicity, large size, cellular uptake and chemical stability [4,5]. Therefore, there is a need to overcome those limitations. By combining any two metals to form a bimetallic nanoparticle, the fascinating and synergetic relationship between them shows new enhanced structural and physical properties, subsequently increasing their functionality and application [2]. In addition, the experimental results have shown a remarkable enhancement capability and a possible solution to overcome the limitation of monometallic nanoparticles.

Bimetallic nanoparticles are attracting more attention in recent years due to their unique physical properties (quantum effect, high surface area, mobility), chemical, mechanical, thermal, optical, catalytic and magnetic properties [6–10]. These properties make

bimetallic distinguishable from their monometallic counterparts and give a superior performance that the individual metals do not have [11–13]. Both mono and bimetallic nanoparticles are suitable for applications in various fields, including biomedical, biosensors, nanomedicine, imaging, wastewater treatment, oil and gas industries, agriculture/food processing and gene/drug delivery [14–20]. In addition, antimicrobial and anticancer activities of bimetallic nanoparticles have also been investigated extensively [21–26].

There are three methods of synthesizing nanoparticles: physical, chemical and biological (Figure 1). Either of the two main approaches can make these methods, namely, the top-down and the bottom-up approach. The top-down approach involves the breaking down of the bulk material by external mechanical force to nanosized particles, e.g., mechanical grinding, ball milling, laser ablation, microwave irradiation, etc. On the other hand, the bottom-up approach involves building the nanoparticles right from the atomic level. Atoms build up to form molecules, then the molecules grow into a cluster and finally create the nanoscale particles. Examples of this method include the sol-gel process, pyrolysis and chemical precipitation [27]. Though the top-down approach is a faster method, there is no control of particle shape and size as compared to the bottom-up approach, where shape and size can be easily controlled by controlling the synthesis parameters such as pH, temperature and concentration. This review will focus on bimetallic nanoparticles, synthesis, characterization, biological and environmental applications and the toxicity of bimetallic nanoparticles.

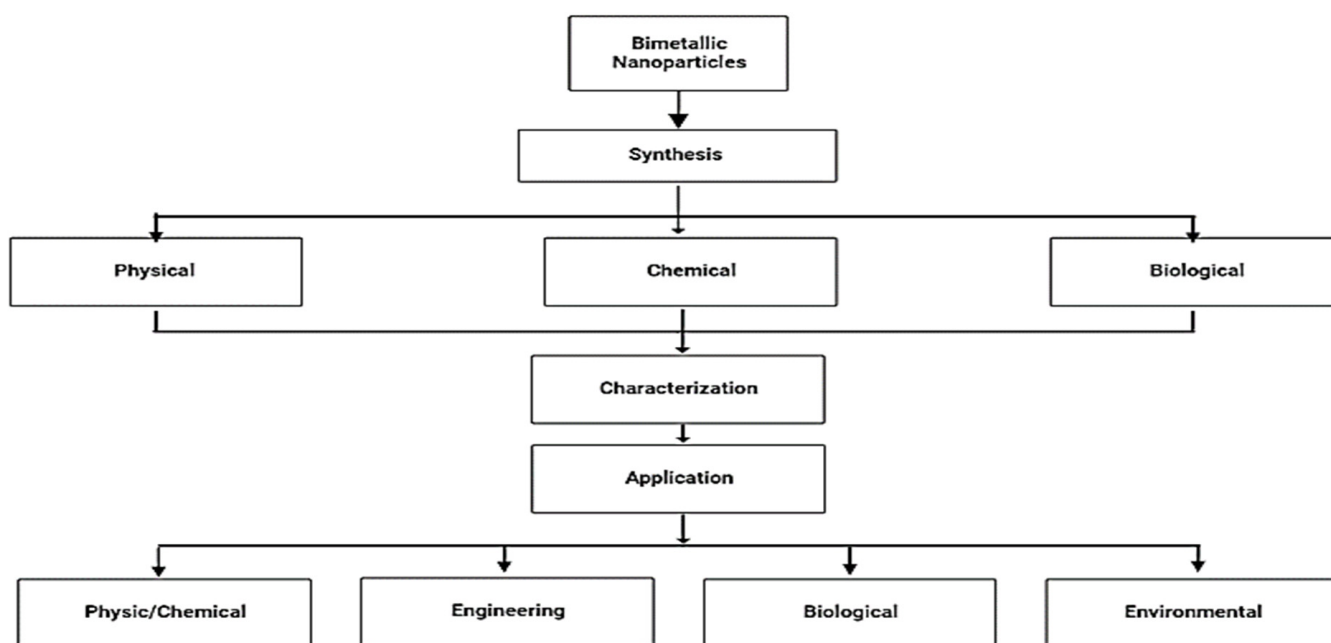


Figure 1. Schematic diagram of bimetallic nanoparticles.

2. Different Types of Bimetallic

Bimetallic nanoparticles are synthesized when two different metals are mixed together in a reaction vessel under optimized conditions, resulting in various structural and morphological changes [28]. Different combinations of metals, including noble and transition metals can produce many different types of bimetallic nanoparticles. These bimetallic nanoparticles can be in many forms, including gold-based, silver-based, copper-based, nickel-based, iron-based, platinum-based or palladium-based bimetallic nanoparticles (Table 1).

Table 1. Summary of the different combinations of bimetallic nanoparticles and the method of synthesis.

Forms of Bimetallic Nanoparticles	Type of Bimetallic Nanoparticle	Structure of the Bimetallic Nanoparticle	Method of Synthesis	References
Gold based	Au-Pt	Cubic crystal structure	Green synthesis	[29]
	Au-Cu	Porus structure	Galvanic replacement	[30]
	Au-Ni	Porus structure	Chemical synthesis	[31]
	Au-Pd	Core-shell	Chemical Synthesis	[32]
	Au-Ag	Alloy & Core-shell	Green synthesis	[33]
Silver based	Ag-Cu	Alloy	Green synthesis	[34]
	Ag-Au	Alloy	Green synthesis	[35]
	Ag-Fe	Spherical shape	Green synthesis	[36]
	Ag-Pd	Cubic crystalline structure	Green synthesis	[37]
	Ag-Zn	Wurtzite hexagonal	Green synthesis	[38]
Copper based	Cu-Ni	Alloy	Sol-gel	[39]
	Cu-Ag	Alloy	Green synthesis	[40]
	Cu-Fe	Classified Janus	Electrical explosion	[41]
	Cu-Co	Spherical	Inverse micellar encapsulation	[42]
	Cu-Pt	Alloy & core	Hydrothermal method	[43]
Nickel based	Ni-Co	Porous	Chemical co-reduction	[44]
	Ni-Fe	Alloy & core shell	Chemical synthesis	[45]
	Ni-Au	-	Physical Synthesis	[46]
	Ni-Pt	Alloy	Co-reduction	[47]
	Ni-Ru	Alloy	Chemical synthesis	[48]
Iron based	Fe-Zn	Spherical	Green synthesis	[49]
	Fe-Ti	Nano-Sphere	Chemical synthesis	[50]
	Fe-Mn	Spheroid-like	Chemical synthesis	[51]
	Fe-Ag	Janus structure	Physical Synthesis	[52]
	Fe-Cu	Crystalline	Green synthesis	[53]
Platinum based	Pt-Ag	face-centred cubic structure	Chemical synthesis	[54]
	Pt-Co	face-centred cubic structure	Chemical reduction	[55]
	Pt-Ni	face-centred cubic structure	Chemical reduction	[56]
	Pt-Pd	Carbon sphere	Chemical reduction	[57]
	Pt-Pd	Crystalline	Green synthesis	[58]
Palladium based	Pt-Fe	Face-cantered cubic	Chemical synthesis	[59]
	Pd-Au	Hexagonal nanoplate	DNA ligand	[60]
	Pd-Ag	Spherical	Green synthesis	[61]
	Pd-Cu	Crystalline alloy	Green synthesis	[62]
	Pd-Zn	Spherical	Chemical synthesis	[63]

3. Synthesis of Bimetallic Nanoparticles

Generally, the synthesis of bimetallic nanoparticles involves either breaking down bulk materials to nanosized particles or building up the nanoparticles from their respective atoms. These two approaches are the top-down approach and the bottom-up approach (Figure 2). The bottom-up approach usually involves mixing two different metal precursors in a reaction vessel under the optimized condition to which a reducing and stabilizing agent is added. However, the general procedure of synthesizing bimetallic nanoparticles can be categorized into three main categories, namely, physical, chemical and biological methods (Figure 3).

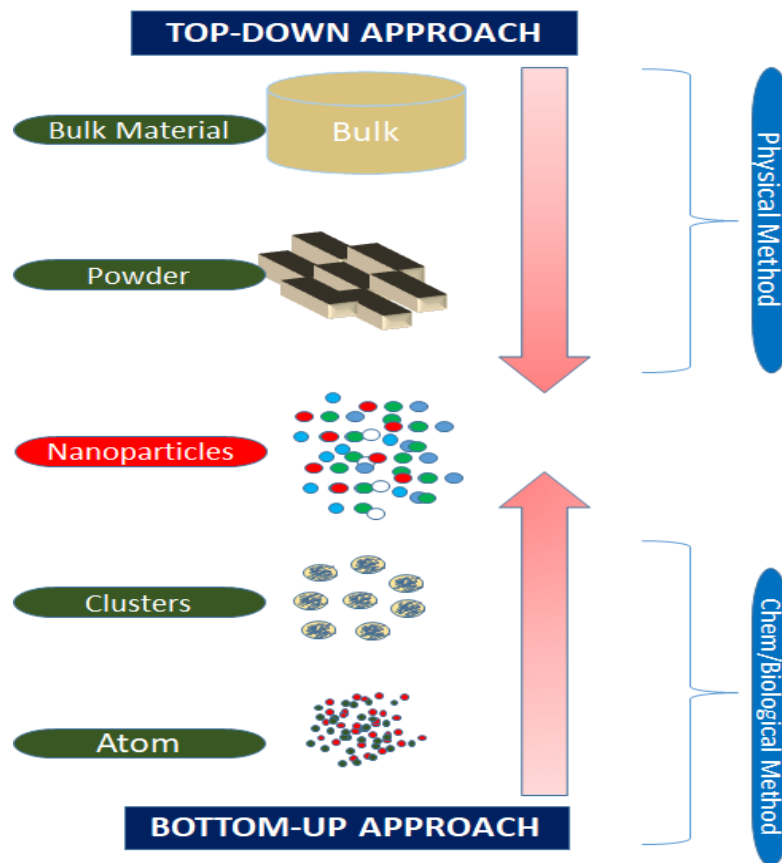


Figure 2. Top-down and bottom-up approach.

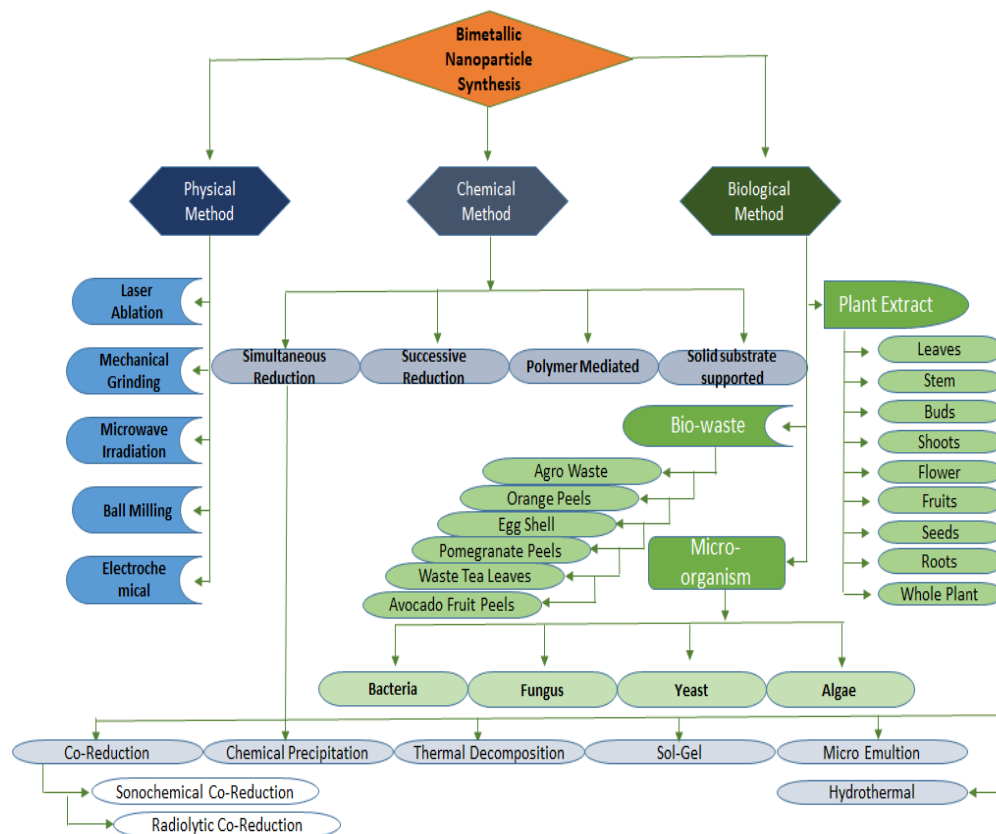


Figure 3. Methods of synthesizing bimetallic nanoparticles.

3.1. Physical Method

The physical method of nanoparticle synthesis generally involves the breaking of bulk materials into fine particles. It has some advantages over the other synthesis methods, such as uniformity in the formation of nanoparticles and less contamination.

3.1.1. Laser Ablation

This is a top-down approach where the bulk material is broken down into nano-sized particles. The process involves irradiating a solid or sometimes a liquid substance with a laser beam to remove particles from their surface. This process can be used to synthesize a well dispersed bimetallic nanoparticle, as reported by [64]. The mechanism of nanoparticle formation using laser ablation method is appropriately explained by [65] and [66], respectively.

3.1.2. Mechanical Grinding

In this process, bimetallic nanoparticles are formed by grinding the mixture of the metal salts with the reducing agent in a solid state. Au–Ag nanoparticles were synthesized by [67] using this method. In a simple two-step experiment, a solid-state mixture of AgNO₃, chitosan and NaOH was first ground using a mortar and pestle and then followed by the addition of a concentrated solution of HAuCl₃ which, subsequently, resulted in the formation of Au–Ag bimetallic nanoparticle.

3.1.3. Microwave Irradiation

Microwave irradiation can also assist in the fabrication of bimetallic nanoparticles and have certain advantages, such as excellent control of the reaction parameters, the heating source having no direct contact with the reactant/solvent and a high heating rate. Microwave heating in this method is used to replace the use of chemicals during the synthesis process. This method synthesized Ag/ZnO bimetallic nanoparticles by heating the mixture of AgNO₃ and ZnO nanoparticles dispersed in ethanol under reflux in a microwave reactor for 20 min [68]. In addition, [69] synthesized Au–Pd and Au–Pt bimetallic nanoparticles using hydrothermal and microwave irradiation.

3.1.4. Ball Milling

Ball milling is a method that grinds materials into extremely fine powders. It consists of a hollow horizontal compartment containing balls made of steel that rotate around its axis. The subsequent rotation crushes the materials inside the compartment into fine particles with the help of the steel balls. This method was used for synthesizing Al–Fe and Ni–Fe bimetallic nanoparticles, as reported by [70] and [71], respectively.

3.1.5. Electrochemical Method

In this method, an electrolyte and an electrically conductive metal substrate are used for the synthesis of bi-metallic nanoparticles. The synthesis occurs at the interface between the electrolyte solution, containing the metal salt precursors and the conductive metal substrate [72]. A study employed this method and synthesized Co–Ni bimetallic nanoparticles that were used to detect tetracycline [73]. Similarly, Bi–Sb and Au@Ag core shells were synthesized by [74] and [75] using the same electrochemical method and used for the reduction of CO₂ and detection of thiram in juice and milk, respectively.

3.2. Chemical Method

The most important factor in the chemical synthesis method is the reducing and stabilizing agent. This method generally involves using a suitable metal source, usually soluble salts or ions that can be dissolved in water. To that solution, a reducing agent in the form of chemical, polymer or ligand is added which strongly affects the nanoparticle particle formation. In some instances, only the stabilizing or reducing agent is required for the synthesis while other processes require both the reducing agent and as well as the stabiliz-

ing agent. When both metal precursors are present and simultaneously reduced during the synthesis process, it can lead to nanoparticle formation, while successive reduction can lead to core–shell formation [76]. The fabrication of bimetallic nanoparticles using the chemical method can be generally grouped into two, namely, simultaneous and successive reduction. Both are simple, fast, economic and can be used for large-scale production, and the doping of other materials during synthesis is possible. Various parameters such as pH, temperature, concentration and rate of irradiation are used to control the chemical synthesis of bimetallic nanoparticles.

3.2.1. Simultaneous Reduction

Co-Reduction

Co-reduction is the simplest method of bimetallic synthesis. It involves the mixing of two metal precursors together. To that mixture, a reducing agent or stabilizing agent is added, which can reduce the metal ion to atoms and stabilize the aggregation process [77]. In practice, polymers can be used to control the reduction and aggregation of bimetallic nanoparticles. The polymer and metal ions can interact after the reduction and vice versa. It is believed that when the reduction of metal nanoparticles comes first, before the interactions, some properties including the size and structural properties can be determined only by the reduction process. However, when the interaction comes before the reduction, the particle size structure may be affected [78]. For example, Fe–Ni bimetallic nanoparticle supported by zeolite was prepared by sodium borohydride— NaBH_4 —for the simultaneous reduction of the corresponding mixture of the two metal salts. In the experiment, the Fe and Ni metal salts precursors were dissolved in an ethanol–water solution and then mixed with zeolite, which acts as the stabilizing agent. Adding the reducing agent— NaBH_4 —to the mixture under vigorous stirring in a dropwise manner causes a black suspension within 30 min, thereby indicating the formation of Z–Fe/Ni bimetallic nanoparticles. Subsequently, Fe–Ni bimetallic nanoparticle was also fabricated by the simultaneous reduction of the same mixture of metal salt solution using the same reducing agent but without the addition of the stabilizing agent ‘zeolite’ [79]. The same process was employed by [80] in synthesizing the same bimetallic nanoparticle supported by bentonite (B–Fe/Ni), which serves as the stabilizing agent.

Sonochemical Co-Reduction

This process involves using high-intensity ultrasound radiation in a solution to create a chemical reaction at the atomic level. When the aqueous mixture is exposed to a high-intensity ultrasound wave, an acoustic cavitation effect is produced where growth occurs in the region of high temperature and pressure. Sonification also leads to the breaking down of molecules that lead to the production of radicals that act as oxidizing and reducing radicals [81]. A study reported that magnetic Ni–Ag nanoparticles supported by graphene oxide were synthesized using ultrasonication of the aqueous solution of AgNO_3 and $\text{Ni}(\text{NO}_3)_2$ [82]. The graphene oxide act as the stabilizing agent while NaOH and hydrazine hydrate (N_2H_4) act as the reducing agent. The mixture of the aqueous solution of the metal salts with stabilizing agent (graphene oxide) was first ultrasonicated for 30 min. Then, the reducing agents (NaOH and hydrazine hydrate (N_2H_4)) were added under N_2 atmosphere at 90°C and the mixture was ultrasonicated again for 10 min. The mixture was refluxed at 90°C for 1 h, then centrifuged and the solid product was removed and washed with ethanol and distilled water before drying at 50°C in a hot air oven. In addition, a polymer-stabilized Au–Pd bimetallic nanoparticle synthesized by ultrasonic irradiation using PVP and ethylene glycol was the stabilizing agent [83].

Radiolytic Co-Reduction

Radiolytic co-reduction is the process of applying ionizing radiation (UV, X-ray, Gamma ray, electron beam, etc.) to an aqueous mixture in order to reduce the ionic solutions to atoms. This method offers some advantages due to the efficient control of

radiation dose delivered to the mixture which, in return, control the structure and growing process of nanoparticles, although in terms of nanoparticles shape the radiolytic process can be difficult to control in the radiolytic co-reduction of metal ion solutions, reducing radicals produced when radiolysis occurs [84]. Moreover, the electron radicals with a high reduction potential replace the chemical reducing agent. The radiolytic co-reduction mechanism involves hydrogen-free radicals and hydrated electrons generated by the radiolysis of water. A study [85] reported a two-step synthesis of platinum-based bimetallic nanoparticles Pt-M (M: V, Mo, W) supported by graphene oxide with the help of gamma-ray irradiation at a rate of 4.5 (kGy/h) under ambient conditions. In the first step, graphene oxide was prepared, while in the second step, the metal source was dissolved in the prepared graphene oxide solution. Exposing this mixture to gamma radiation reduces the mixture and produces Pt-V, Pt-Mo and Pt-W bimetallic nanoparticles. Further, another study [86] reported that a low exposure rate can reduce gold and silver ions, thereby producing a gold core silver-coated bimetallic nanoparticle but, in contrast, a high dose rate can produce alloyed Ag-Pt bimetallic nanoparticles. Other types of bimetallic nanoparticles that were produced using gamma irradiation include Ag-Pt [87], Au-Cu [88], Pd-M (M = Ag, Au, Cu, Ni, and Pt) [89], Pt-M (M = Au, Cu, Ni) [90], Pd-Au-Ag tri-metallic nanoparticle [91] and Pt monometallic, Pt-Ru bimetallic, Pt-Ru-Sn, Pt-Ru-Mo trimetallic and Pt-Ru-Mo-Sn tetra-metallic nanoparticles [92].

Chemical Precipitation

Chemical precipitation is an easy, single step and fast method of synthesizing nanoparticles. It involves converting dissolved substances in a solution into an insoluble solid, thereby making the solution a super saturated one. The insoluble solid that is formed is known as the "precipitate". In terms of synthesizing a bimetallic nanoparticle, it is often regarded as "co-precipitation" due to the fact that two metal salts form the precipitate. Fe-Mn bimetallic have been synthesized using co-precipitation method [51]. The metal precursors were first prepared individually in the presence of excess oxygen and then mixed in an Erlenmeyer flask at 70 °C while stirring at 50 rpm. The pH of the solution was adjusted to 9 by adding 10% NH₄OH while mixing continues for 4 h. The solution was left in a stationary condition until the precipitate was formed. The precipitate was separated by centrifugation, washed and finally dried in hot air oven at 50 °C until constant weight was reached. Then, the final product was stored in a desiccator. hBN-Fe₃O₄ [93], Me-Mn (Me = Co, Ni, Sn) [94], Fe-Ti [50], CoCu-Mof [95] and Fe-Cr bimetallic nanoparticles have also been synthesized using this method.

Thermal Decomposition

Thermal decomposition is a chemical reaction that occurs when a compound breaks down at high temperature. It is known that metal nanoparticles, especially the noble metals, can be synthesized at room temperature through the action of the reducing agent that reduced the corresponding metal salts. However, some metal nanoparticles such as transition metals, require a higher temperature during synthesis because of their inability to be crystallized at room temperature [96,97]. To synthesize bimetallic nanoparticles using this method, the temperature of the reaction must be increased to or near decomposition temperature. The metal precursor with lower decomposition temperature will be decomposed (reduced) first and form a single-component monometallic nanoparticle, while the second metal precursor is still in the solution. When the decomposition temperature of the second metal precursor is reached, it will be decomposed and formed on the surface of the first metal nanoparticle, thereby forming a bimetallic nanoparticle. For example, synthesis of bimetallic titanium complexes M-Ti-O (M = nickel—Ni, Cobalt—Co, Manganese—Mn) from cobalt, manganese and nickel metal precursors by using the thermal decomposition method were reported in the literature [98]. In addition, the thermal decomposition method of synthesis has been used to synthesize Pd-Ir, [59], Co-Mn [99], Pd_xNi_y [100], Ti/Ce-Sb-SnO₂NFs and Pd-Ag/C bimetallic nanoparticles [101].

Sol-Gel Method

Sol-gel method is a simple, cheap and fast method of fabricating nanoparticles. It is a technique based on colloidal chemistry, where a liquid mixture is transformed into a gel. To synthesize nanoparticles, the metal precursors are first converted into a “sol” form or colloidal suspension through hydrolysis and polymerization and then subsequently converts into “gel” by gelation. The sol-gel formation process involves four stages: hydrolysis, condensation, growth and agglomeration of particles [102]. A study reported synthesis of alloyed Cu–Ni bimetallic nanoparticles using sol-gel method [39]. The metal precursors were mixed with citric acid and stirred at room temperature until transparent solution is obtained. While stirring continues, ethylene glycol was added, and the mixture was evaporated at 130 °C for 24 h to obtain dry precursor and then calcinated at 700 °C to obtain the final product. The magnetic properties were studied using SQUID magnetometry and the Cu–Ni bimetallic nanoparticle shows a ferromagnetic behavior. Other bimetallic nanoparticles synthesized using sol-gel method include Mg–Al [103], Pt–Pd [104], and Au–M (M = Ag, Pd, Pt) [105].

Micro-Emulsion Method

Micro-emulsion is a homogeneous, isotropic and thermodynamic stable solution that contains at least 3 components: a polar domain (usually water), non-polar domain (usually oil) and a surfactant (ionic or non-ionic). This solution is macroscopic in nature and the surfactant molecules usually form a tiny film that separate the polar and non-polar phase. Different types of micro-emulsion include water-in-oil (reverse micelles), oil-in-water (O/W), bicontinuous and supercritical CO₂ microemulsion. Among the different types of microemulsion, water in oil microemulsion is mostly used for nanoparticle synthesis while only a few nanoparticles are synthesized using the oil-in-water microemulsion method [106,107]. In a study, Ag–Au bimetallic nanoparticle was prepared using the water-in-oil microemulsion (reverse micelle) method [108]. The Ag and Au metal precursors were reduced at room temperature using sodium-bromide—NaBH₄[−] as the reducing agent in water-in-oil microemulsion containing TrionX100, water and cyclohexane and 1-hexanol as the surfactant, respectively. The solution was mixed by continuous stirring and a color change was immediately noticed after the formation of the bimetallic nanoparticle. Zn–Se [109], Au–Pd [36], Au–Pt [110], Au–Ag [111], Pd–Ir [112], N–Mo [113], Cu–Ni [114], and Pt–Ru bimetallic nanoparticles [115] were synthesized using water-in-oil microemulsion method while Ag–AgCl [116], Ag@AgCl [117], Ag@AgBr surface-sensitize Bi₂WO₆ [118], Mn–Zn [119], Zn-doped TiO₂ [120], and Cu–Ce [121] were synthesized by the oil-in-water microemulsion method, respectively.

Hydrothermal Reduction Method

The hydrothermal method is a convenient method of synthesizing nanoparticles at very high temperature and pressure. The properties of the nanoparticles can be controlled by regulating the pH, temperature and pressure of the synthesis medium. Some advantages of this method are that pure products without contamination can be produced, and thus a high yield production of high quality nanocrystal can be obtained and it offers the ability to control some properties of nanoparticles such as chemical and physical properties. However, the high cost of equipment is always a challenge while the process of crystal growth cannot be monitored. A study reported [122] synthesis of bimetallic Pd–Au alloy nanocatalysts using the hydrothermal method. In a typical experiment, the aqueous mixture of metal precursors was heated at 180 °C in a stainless-steel autoclave for 12 h. The final product was centrifuged, washed and redispersed in ethanol for further use. Additionally, microwave-assisted hydrothermal synthesis of Cu–Co embedded in nitrogen doped carbon (CuCo–N/C) was also reported [123]. In addition, other bimetallic nanoparticles were synthesized using this method, including Au–Pt and Au–Pt [69], Ni–Cu [124,125], Ce–Fe [126], Co–Ni [127], Pt–Pd [128], Pt–Ru [129], Ti–Zr [130], Pd@Au [131] and multi-walled carbon nanotube Ni–Mn–S tri-metallic nanoparticle.

3.2.2. Successive Reduction

Successive reduction (also referred to as seeded growth or seed mediated growth) is a sequential reduction approach whereby the first metal precursor is reduced to metal atoms (the seed), then the second metal precursor is added and subsequently reduced on the surface of the first metal thereby forming a bimetallic nanoparticle in form of clusters, crystals or core–shells. However, some metals are nobler than others. For example, in the synthesis of Au–Ag nanoparticles, if the aqueous solution of Au^{3+} is first reduced to gold nanoparticles, the subsequent addition of the aqueous solution of Ag^+ in the presence of sufficient reducing agent will lead to the formation of a bimetallic that has a gold core—which is the seed and a silver shell. However, the reverse is not always the case. Assuming that Ag^+ is reduced first to silver nanoparticles, the subsequent addition of Au^{3+} will most likely form a hollow nanoparticle where the silver core is completely dissolved. This happens because gold is nobler than silver and the cations of the noble gold oxidizes the silver core and deposited on the surface of the dissolving silver nanoparticle [76]. Galvanic replacement reaction is a technique that is mostly used to prepare hollow metallic nanostructures and it is widely used to fabricate core–shell bimetallic nanoparticles. Synthesized core–shell and seeded grown bimetallic nanoparticles include Au–Ag bimetallic nano-boxes [132], Pd–Cu [133], Pd–Au nano-cubes [134], Au–Pd [135,136], Au–Ag [137], Pd-core Au–Pt shell tri-metallic [138] and Au–Pd core Pt shell tri-metallic nanoparticles [139].

3.3. Polymer Mediated Approach

Bio-compatible polymer has also been used to synthesize bimetallic nanoparticles. Bio-compatible polymers are capable of interacting with biological systems without causing an adverse effect. Bio-compatible polymers are of two categories: natural and synthetic polymer. Natural polymers are derived from a natural source such as polysaccharides, nucleic acids and proteins. Examples include chitosan, collagen and hyaluronic acid. Synthetic polymers, on the other hand, are chemically synthesized and tailored to meet specific requirement for various biomedical applications. Some of the examples include PLGA–poly (lactic-co-glycolic acid), PEG–polyethylene glycol, and polyurethanes. Both natural and synthetic polymers have been used to synthesize various types of bimetallic nanoparticles. For instance, a study reported [140] the synthesis of Ag–Au by using poly diallyldimethyl ammonium chloride (PDADMAC) as the stabilizing agent. The Ag–Au bimetallic nanoparticle was found to be 2–20 nm in size and also possess good catalytic activity. Cu/Ag was also synthesized by using hydrazine and gelatin as the stabilizing agent [141]. Carboxymethyl cellulose coated Fe–Cu bimetallic nanoparticles was synthesized [142] to prevent aggregation and removal activity of Cr(VI). A comparative assessment of the bimetallic nanoparticles was carried out pre and post being coated with carboxymethyl cellulose to evaluate the role of stabilization method and it was found out that the removal efficiency of the coated nanoparticle was lower as compared to the uncoated particle. This was attributed to the electrostatic repulsion between the stabilized nanoparticles and Cr(VI) species. Similarly, PEG was used to stabilize Ni–Fe for the removal of Cr(VI) [143]. It was observed that more than 99% of Cr(VI) was removed from the solution in about 60 min. The excellent performance of the bimetallic nanoparticle was linked to the strong adsorption, reduction and co-precipitation of the PEG-coated Ni–Fe. Ru–Co was also stabilized by PEG and used as an efficient heterogeneous catalyst for Suzuki–Miyaura cross-couplings [144]. Bimetallic nanoparticles revealed excellent catalytic activity with a conversion rate of up to 100%. It also maintains its catalytic activity for up to 6 catalytic cycles. PLGA@Au–Ag loaded anticancer drug was synthesized by [145]. Paclitaxel (PTX) anticancer drug was loaded into PLGA and a shell of Ag formed through controlled reduction by PVP was used to coat the PLGA forming PLGA@Ag nanoparticle. The PLGA@Ag was then used to grow Ag–Au nanoshell on the PLGA, thereby forming a PLGA loaded PTX core and Ag–Au shell hybrid. Surface enhanced Raman Spectroscopy experiments showed that PTX-loaded PLGA@Ag–Au has the potential to provide a desirable SERS optical tag for biomedical imaging, controlled anti-cancer drug

release and hyperthermal effect. It also has the potential to be used as a new theranotic for detecting and treating cancer effectively. Fe–Cu and Fe–Ni chitosan stabilized bimetallic nanoparticles were synthesized by [146] and [147], respectively. The former was found to be highly effective for the removal of chromium from wastewater, while the latter was found to be very effective for the removal of organic contaminants such as amoxicillin and heavy metals including Cd(II). The role of collagen concentration in stabilizing Ag@Au bimetallic nanoparticles was also investigated by [148].

3.4. Solid-Supported Bimetallic Nanoparticles

These are a class of bimetallic nanoparticles that are supported on a solid substrate such as silica, alumina or carbon. The bimetallics are usually adsorbed on the surface of the substrate, thus increasing their stability and durability and preventing aggregation or detachment from the surface. Solid-supported bimetallic NPs have been widely used in various catalytic reactions, such as hydrogenation, oxidation and reduction reactions. For example, Pt-based bimetallic NPs supported on carbon have been used as efficient catalysts for the hydrogenation of aromatic compounds such as benzene and toluene [149]. Pd–Au supported by mesoporous silica have been used as high performance catalyst for the hydrogenation of cinnamaldehyde [150]. Ni–Fe supported by activated carbon was synthesized by [151] and used for the hydrogenation of biomass-derived ethyl levulinate into γ -valerolactone. Similarly, Pd-based bimetallic NPs supported on silica have been used as efficient catalysts for the selective oxidation of alcohols to aldehydes [152]. In addition to catalysis, solid-supported bimetallic NPs have also been investigated for their potential applications in other fields, such as electrocatalysis and sensing. For example, Pt-based bimetallic NPs supported on carbon have been used as efficient electrocatalysts for the oxidation of methanol in fuel cells [153]. Similarly, Au-based bimetallic NPs supported on silica have been used as efficient sensors for the detection of heavy metal ions [154].

3.5. Biological Method

Usually, synthesizing nanomaterials via physical or chemical method is expensive, tedious, time consuming, and hazardous to the ecosystem, and further, they produce highly toxic by-products, require a high energy demand and pose a potential threat to human health. Therefore, there is a need to find a more biocompatible, fast and cheap synthesis approach that can overcome these limitations. The biological method of synthesizing nanoparticles, also termed the ‘green synthesis method’, is an alternative and more biocompatible approach to fabricating nanomaterials. The green synthesis method involves producing nanoparticles without the use of hazardous or expensive chemicals. Instead, natural sources are used to produce the nanoparticles and the end product is more environmentally friendly and biocompatible. Generally, biological synthesis can be done in two ways, by using plants (i.e., leaves, stem, fruits, seeds, bark, peels, shoots, roots, etc.) as the reducing and stabilizing agent or microorganisms (bacteria, fungus, yeast etc.). Nanoparticles synthesized by this approach are often referred to as biogenic nanoparticles/nanomaterials [6].

3.5.1. Microbial Synthesis Method

This method involves the use of microbes, especially bacteria, fungi or yeast to synthesize nanoparticles by an intracellular or extracellular mechanism. For the intracellular mechanism, ions are transported into the cell of the microorganism with the help of intracellular enzymes (endo-enzymes), and thus nanoparticles can be formed. As for the extracellular mechanism, it involves metal ions binding or adsorption on the surface of the cell and subsequent reduction occurs in the presence of extracellular enzyme or exo-enzyme. Among these two mechanisms, extracellular is preferred because in intracellular mechanism, further downstream processing is required in order to recover the synthesized nanoparticles. The recovery process involves breaking the cell wall of the microorganism in order to retrieve the nanoparticles and subsequent washing, and centrifugation

steps are required to purify them. Numerous research studies have reported on synthesis of monometallic nanoparticles using bacteria. However, there are very few reports on bimetallic synthesis. For example, a study reported [155] synthesis of Pd–Pt bimetallic nanoparticle by using *Shewanella oneidensis* MR-1 bacteria and reduction occurs via the extracellular mechanism. Bacteria were able to reduce the aqueous mixture of the metal ions after incubation for 24 h at 30 °C. The final product was washed, centrifuged and resuspended in Milli-Q water for subsequent assays. Similarly, Pd–Ag, Pd–Au and Pd–Pt bimetallic nanoparticles have been synthesized using *Shewanella oneidensis* MR-1 [156–159]. Core–shell Au–Pd, Au–Ag and Pd–Ru bimetallic nanoparticles have been synthesized using *Escherichia coli* [160–162]. Au–Ag alloy have been synthesized by using *Lactobacillus* strains and *Spirulina platensis*, respectively [163,164]. A study reported synthesis of Ag–Cu bimetallic nanoparticles using the fungal strain—*Aspergillus terreus* [164]. The fungal biomass was mixed with the aqueous solution of the metal salts and then kept under stirring in a microwave for a specific time duration. The precipitate was collected and washed multiple times before being calcinated at 450 °C to obtain the final product. In addition, Au–Ag and Au–Ag alloy nanoparticles were also synthesized using filamentous fungus *Neurospora crassa* [165] and *Fusarium oxysporum* [166], respectively. Regarding yeast mediated synthesis, most of the synthesized nanoparticles using this method are monometallic nanoparticles such as gold and silver [167], but there are limited reports on bimetallic nanoparticle synthesis. However, a study reported synthesis of Au–Ag alloy by using instant dry yeast [168]. Ag–Au was also synthesized by using algae [169].

Other microorganisms such as viruses and macromolecules such as proteins and DNA have also been used in synthesizing bimetallic nanoparticles [170]. Recently, a report suggested [171] fabrication of Au–Ag bimetallic nanoparticle using viral strain *Squash leaf curl China virus* (SLCCNV) isolated from a plant species. Likewise, protein and DNA mediated synthesis of Au–Ag and CuO–NiO bimetallic nanoparticle were also reported [172,173].

3.5.2. Plant Mediated Synthesis

There are many nanoparticles including mono, bi, tri and quad metallic nanoparticles that have been synthesized via plants. Plant mediated synthesis offers various advantages which makes them more suitable and a better approach than microbial synthesis. It uses plant extracts which act as a reducing and stabilizing agent. It also eliminates the need for bacterial culture medium while offering a faster synthesis route and better control of the nanoparticle size and morphology. It is believed that different phytochemicals found in the plant extract are responsible for reducing and forming nanoparticles (nano-phyto-technology). They include proteins, carbohydrates, vitamins, amino acids, flavonoids, alkaloids, terpenoids, ketones, tannins, aldehydes, amides, polysaccharides, polyphenols, carboxylic acid and phenolic acid [174,175]. The main controlling factors during synthesis of bimetallic nanoparticles using plant extract are the pH of reaction mixture, reaction time, reactant concentration, temperature, concentration of the plant extract and metal salts. These same factors also affect the size and morphology of nanoparticles during synthesis [173]. Several research articles reported the use of different types of plant parts to synthesize bimetallic nanoparticles. A study reported the synthesis of Ag–Au alloy nanoparticles using Kolanut extract [174]. The synthesized nanoparticle was 17–91 nm in size, has spherical morphology and possesses antimicrobial, larvicidal, catalytic and anticoagulant properties. *Kigelia africana* fruit was used to synthesize Cu–Ag by [175,176] at 120 °C under reflux. The nanoparticle was 10 nm in size and inhibits the growth of gram-positive and gram-negative bacteria more than the antibiotic used in the study. Green/red cabbage was used to synthesize Ag/Au alloy/hollow nanoparticles by [177] through a straightforward approach by simply adjusting the pH of the aqueous medium. The vegetable extract act as both reducing and stabilizing agents and the synthesized nanoparticles were 25 nm in size with spherical shape. *Moringa oleifera* leaf has also been used to synthesize Ni/Fe₃O₄. The nanoparticles were synthesized under vigorous stirring

at 70 °C and they were of spherical shape with the size ranging from 16–20 nm [178]. In another study [179], Fe/Pd was synthesized using grape leaf. Equal ratio of the metal precursor and extract were mixed thoroughly for 30 min at room temperature and the nanoparticles were found to be spherical in shape between the size of 20–100 nm. Neem leaf was used to synthesize Au core–Ag shell by mixing an equal ratio of metal precursor in neem leaf broth [180]. The nanoparticles were found to be 50–100 nm in size, and spherical in shape. Mahogany was used to synthesize Au/Ag at room temperature and both metal precursors were reduced simultaneously by the mahogany leaf extract at pH 8.5 and 12.5, respectively [181]. Cashew leaf extract was used to synthesize Au–Ag nanoparticles and by effect of the quantity of the extract, pH and temperature were also observed [182]. Fe/Pd was synthesized using green tea which acts as a reducing/capping agent [183]. Date palm tree leaves are also used for synthesizing bimetallic nanoparticles. A study reported [184] Cu–Ag synthesis using aqueous extract of date palm tree by heating at 95 °C with constant stirring for 1 h, and the nanoparticles obtained were about 26 nm in size. Synthesis of Au–Ag at room temperature using fruit juice pomegranate was also reported [33]. The bimetallic nanoparticle was synthesized via simultaneous reduction and were found to be effective in degradation of methyl orange dye. *Aloe vera* leaf was also used to synthesize Ag–Cu on cotton fabric that can be used for dressing wounds [185]. Fenugreek, coriander and soybean leaf were used to synthesize Au–Ag nanoparticles by mixing equal proportion of the extract and metal precursors after heating at 80 °C for 30 min [186], and chebulic myrobalan was used to synthesize Ag–Pd at room temperature under constant stirring [37]. A detailed list of bimetallic nanoparticles synthesized using different parts of plant extracts from shoots, leaves, stem, roots, buds, fruits, seeds, flowers and whole plants have been reported by [187].

3.5.3. Bio-Waste Approach for Synthesizing Bimetallic Nanoparticles

Biological waste is a rich source of phytochemicals that can also be utilized in synthesizing nanoparticles. The concept involves utilization of waste biomaterials which are sustainable sources for synthesizing nanomaterials and simultaneously remediating environmental pollution. Waste materials used in synthesizing bimetallic nanoparticles include agro waste. A study reported [29] synthesis of Au–Pt by utilizing paddy straw, which is an abundant agro waste to grow nutritionally and medically rich oyster mushroom *Pleurotus florida* (pf), which is further used as a reducing agent to synthesize bimetallic nanoparticle. It was found that the synthesized bimetallic nanoparticle possesses anticancer activity. Another study reported [30] synthesis of Au–Cu bimetallic nanoparticle supported on nano P zeolite modified carbon paste electrode for the detection of hydrazine. The agro waste material–stem sweep ash (SSA) was used as a starting material for silica source for the synthesis of nano P zeolite. The construction of Au–Cu/NPZ/CPE was done via Galvanic replacement technique and the sensor represented favorable analytical properties such as rapid response time, high sensitivity and wide linear range. Graphene oxide supported Au–Pd bimetallic nanoparticle with a core–shell morphology was synthesized by using water extract of pomegranate ash (WEPA) [32]. The core–shell structure of Au–Pd/rGO made a positive contribution in achieving the Suzuki coupling reaction in a very short time. Another agro waste (*Amaranthus tricolor*) was used as a reducing and stabilizing agent to synthesize Ag–Cu bimetallic nanoparticle [29]. The synthesized nanoparticles were found to be very useful for optical sensing of dimethoate. Lemon pomace waste was used to synthesize activated carbon Fe–Zn and the synthesized nanoparticle were utilized as catalyst for the degradation of reactive red 2 (RR2) and azo-dyestuff with a heterogeneous fenton-like reaction. The optimum decolorization condition were pH 3.0, 50 nM H₂O₂ concentration, dye concentration 100 mg L⁻¹, catalyst concentration of 0.1 g L⁻¹ and temperature of 25 °C [49]. Orange peels extract was used to synthesize Au–Pd nanoparticles through a two-step reduction process. The extract serves as a reducing and stabilizing agent. The synthesized nanoparticle showed a color change from light to dark brown in the presence of different concentrations of formaldehyde. This suggests that the synthesized

nanoparticle can be used for formaldehyde sensing [188]. Pomegranate peels was used to synthesize Ni–Fe and they were tested for tetracycline removal and its efficiency was about 93% [189]. Waste tea leaves was used to synthesize Ag–Au [190]. It was found that synthesized nanoparticles can efficiently degrade congo red and 4-nitrophenol in water and in the presence of sodium borohydrate within 6 and 7 min. Avocado fruit peels has also been used to synthesize Ag–Au alloy [191] and synthesized nanoparticles were found to possess antimicrobial and antioxidant properties. Eggshell and cobalt nitrate was used to synthesize Co–Ca bimetallic nanoparticles. They were found to be efficient in the removal of norfloxacin by activating peroxymonosulfate at wide pH 3.0–9.0 in 35 min, and the degradation efficiency was over 90% [192]. NiO–ZnO was also synthesized by using eggshell membrane as template to control the size of the nanoparticle [193]. The synthesis involved a two-step process, i.e., soaking, followed by calcination method. The synthesized nanoparticles were tested for antibacterial and antifungal activity. The result indicated that cell growth was inhibited even at the lowest concentration. Water chestnut peel was used to synthesize Au–Ag bimetallic nanoparticles and synthesized nanoparticles were exposed to various cancer cell lines (HeLa, HCT116 and MDA-MB-231). It was found that bimetallic nanoparticles induced cytotoxicity effectively at 200 ug/ML. Au–Ag bimetallic nanoparticles exposed cancer cells and exhibited apoptotic effects, including mitochondrial membrane potential loss and nuclear condensation [194]. Mahau seeds were used to synthesize Au–Ag [195]. The seed extract contains a family of seven flavonoid fraction which was used as the reducing agent for the synthesis of the bimetallic nanoparticles. The bimetallic nanoparticle was found to be effective in the enhancement of wound healing bio-efficacy. Waste silkworm cocoon has also been used to synthesize Fe/Cu alloy nanoparticles [196]. Silkworm cocoon is a by-product of the silk industry. The cocoon is rich in protein and the extract made from it serves as the reducing as well as stabilizing agent. The synthesized nanoparticles were tested for their antimicrobial activity against selected bacteria strains and fungal pathogens. The result indicated significant antimicrobial activity, which suggested that the nanoparticles can be used as protective agents in cement mortars that can inhibit the growth of pathogens of environmental concern, therefore avoiding early ageing of the mortar. Although it is a known fact that green synthesis approach has some limitations, it still offers an alternative for nanoparticle development due to the rising environmental pollution [197].

4. Characterization Techniques of Bimetallic Nanoparticles

The molecular architecture of nanoparticles such as shape, size, structure, stability, chemical composition, crystallinity and surface interaction plays an important role in figuring out the behavior, characteristics and properties of nanomaterials (Table 2). By analyzing the individual atoms, the nature and type of bond that exist between various atoms can be deduced. Similarly, when the properties of the individual atoms are known, the characteristics of the bulk counterpart can also be predicted. There are various characterization techniques available for nanoparticles depending upon the measurand.

Table 2. Different methods of characterization of bimetallic nanoparticles.

Properties	Features	Techniques	Reference
Morphology	shape, size, structure	DLS, TEM/SEM, STM, XPS, AFM	[198–204]
Topology	Chemical bonding/composition, physical properties, crystallographic structures	XRD, TEM, zeta potential, Brunauer Emmett Teller (BET)	[204–206]

Table 2. Cont.

Properties	Features	Techniques	Reference
Chemical properties	Surface energy, chemical potential, oxidation process, catalysis, functionalization of nanostructures	UV-vis, EDXS, FTIR	[207,208]
Electrical properties	Conductivity, resistivity, dielectric permittivity	AC/DC conductivity, electrokinetics (zeta potential/cyclic volumetry studies)	[209–211]
Optical properties	Absorption, reflectance, luminescence, phosphorescence	Microscopy, FTIR, UV-vis, DPCS, Raman spectroscopy, surface plasmon resonance.	[212,213]
Mechanical properties	Hardness, plasticity, young modulus	AFM, thermomechanical analysis	[214–216]
Magnetic properties	Magnetism	VSM, SQUID, MFM	[217–219]
Thermal properties	Heat flux, change of temperature, volatiles	DSC, EGA, TGA, DTA	[220,221]
Biological properties	Anti-microbial, biodegradability, toxicity	In vitro cell viability, in vivo microbial colony viability	[222,223]

5. Applications of Bimetallic Nanoparticles

Bimetallic nanoparticles are very crucial due to their unique and synergetic properties which are distinguishable from their individual counterparts. Several research articles have reported wide range of applications of bimetallic nanoparticles which were fabricated through physical, chemical or biological method. Bimetallic nanoparticles have application in many fields including biological applications (in medicine and agriculture), environmental application (in water treatment and removal of toxic contaminants), engineering application (in nanosensors, nanochips and nano-semiconductors), and chemical and physical application (in optics, catalysis and paints) (Figure 4).

5.1. Biological Applications

Bimetallic nanoparticles have found numerous applications in medicine, including diagnostic (bio-imaging), therapy (cancer therapy) and preventive (antimicrobial, antioxidant, antidiabetic drug delivery) medicine (Table 3). The highly magnetic properties of Au-Fe and Ni-Co bimetallic nanoparticles makes them suitable to use as contrast agent for CT and MRI diagnosis/prognosis imaging [224] and theranostic agent for tumors [225]. Similarly, Cu-Fe have been used for enhanced chemodynamic therapy [226], Pd-Pt, Au-Co, Au-Co, Ag-Cu, Au-Pt have been used for cancer therapeutics and anticancer activity [21,227–230] and Au-Bi have been used for the inhibition of tumor cells [231]. In preventive medicine, the use of bimetallic nanoparticles is quite extensive and many of them are used as antimicrobial agents, antioxidants, antidiabetic, anti-Alzheimer, anti-inflammatory and drug delivery.

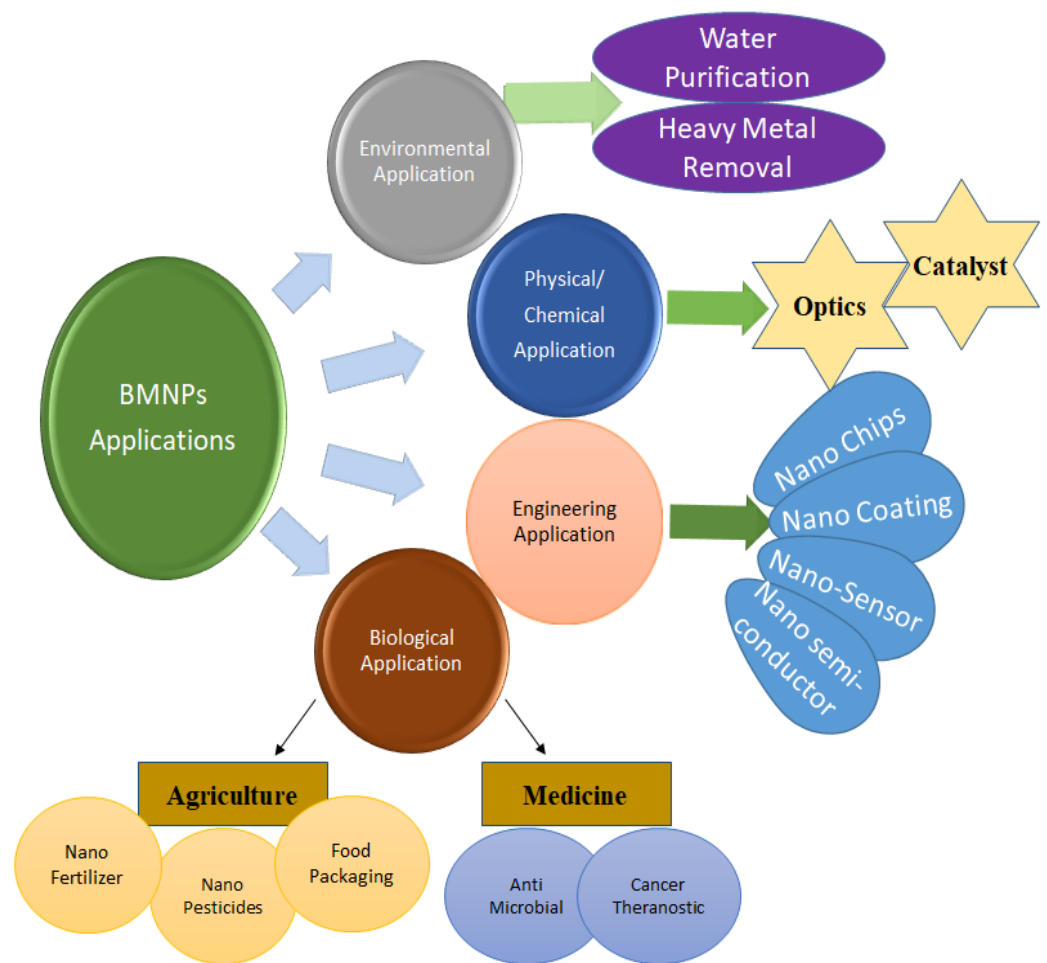


Figure 4. Various applications of bimetallic nanoparticles.

Table 3. Biological applications of bimetallic nanoparticles.

Application	Bimetallic Nanoparticle	Reference
Antimicrobial agents	Pd–Pt	[21]
	Ag–Fe	[28]
	CuO–NiO	[232]
	Ag–Au	[23,169,174,233]
	Cu–Ag	[176]
	Ag–Cu	[234]
	Au–Pt	[235]
	Cu–Zn	[236,237]
Antioxidant	CuO/NiO	[232]
	Ag–Cu	[228]
	Au–Ag	[233]
	Mn–Cu	[238]
	Pt–Pd	[239]
	Ag–Au	[240]
Antidiabetic	Au–Ag	[241]
	Ag–Au	[242]
	Ag/ZnOVI	[243]
	Ag–ZnO	[244]
Anti-Alzheimer	Ag–Au	[242]

Table 3. Cont.

Application	Bimetallic Nanoparticle	Reference
Anti-inflammatory	Ag/ZnOVI	[243]
	Zn-Fe ₂ O ₄ ,	[245]
	CuFeO ₂ ,	[246]
	Au@Ag	[247]
Drug delivery	Au@Pd	[248]
	Au-Pt	[249]
	Pd-Pt	[250]

5.2. Agriculture

The agricultural sector has been challenged with numerous pathogens, insufficient soil nutrients and pests that affect the growth of plants and the storage of crops, resulting in poor yield of food crops while causing food security problem. Although many approaches such as using different types of pesticides and herbicides have been applied in combating plant disease, weeds and pests. However, there is an ecological concern regarding pesticides and herbicides toxicity to the environment. Hence, there is a need for more biocompatible alternatives that are less harmful to human, plants and animals. Due to their synergetic and distinct properties, bimetallic nanoparticles have already found their applications in the agricultural sector. Bimetallic nanoparticles such as Fe-Mn and Zn-Fe have been used as nano-fertilizer to influence the growth of lettuce seedlings [251] and chickpea [252]. Synthesized Cu-Zn nano-fertilizer can also serve as a micronutrient source for plants [253]. Similarly, synthesized Cu-Zn, ZnO-TiO and Ag-Ni bimetallic nanoparticles have been used as nano-pesticide/insecticide against cotton Mealybug [254], *Spodoptera frugiperda* (an important pest of several crops) [255] and *Lymphatic filariasis* Vector [256]. In addition, Au-Pd have also shown larvicidal activity against mosquito larvae [257]. Another application of bimetallic nanoparticles in agriculture is food packaging. In order to increase the life span of food stuffs, it is necessary that the packing material should possess the ability to block CO₂, oxygen and moisture/water vapors. It is also necessary for effective transportation and preservation. In addition, the packing material should possess some properties such as biodegradability, antimicrobial activity, thermal and chemical stability, mechanical strength and recyclability [18]. Bimetallic nanoparticles used in active food packaging include Ag-TiO [258], ZnO-Ag [259] and Ag-Cu [260,261].

5.3. Environmental Application

The contamination of water bodies by heavy metal ions and dye discharge from various industries around the world have aroused concerns regarding human health. Dyes discharged from industries are known to be toxic for human organs such as liver and kidney [262]. However, there is a need to purify and remove the various contaminants from bodies of water. Bimetallic nanoparticles have been used for this purpose. A study reported that Fe-MgO is able to remove heavy metal ion and dye from water [262]. Ag-Au [263,264], Fe-TiO [265] and Pt-Ag [266,267] have been used for 4-nitrophenol reduction, Cu-Ni have been used for dye degradation and reduction of hazardous pollutants [268–270], Cu-Pt have been found to reduce nitrate to ammonia [270], Fe-Ni have been used for the removal of profenofos organophosphorus pesticide [271], Fe/Ni have been used for simultaneous removal of nitrate and phosphate, antibiotics and arsenic (V) from mine water [79,80,272]. Fe-Ti was used for the removal of fluoride from drinking water [50]. Fe-Mn and Co-Fe have also been used as antifouling agent to prevent corrosion or reduce the growth or speedup the detachment of the subaquatic organism that usually stick at the bottom or hull of a vessel and also affect its performance [273–275].

5.4. Engineering Application

The fascinating properties of bimetallic nanoparticles have made them to be suitable for various engineering applications. Bimetallic nanoparticles have been used in the

fabrication of nanosensors, nanochips, nano semiconductors and nanocoating. For example, Ag–Cu, Au–Cu, Fe–Mn, Pd–Ru, Ag–Cu, Co–Ni, Au–Ag, Au–Pt, Cu–Sn and Pd–Au bimetallic nanoparticles have been used to fabricate sensors/biosensors that can sense dimethoate [34], hydrazine [30] and detect *Salmonella typhimurium* in milk samples [275], as well as an anti-cancer drug [276], anti-inflammatory drug 4-aminoantipyrine [277], luteolin [278], favipiravir [279], diclofenac [280], glucose in serum [281] and coal mine gases sensor [131]. For detecting pesticide contaminants in the environment, many bimetallic nanoparticles have been used including Ag–Au, Au–Pd, Au–Pt, Au–Ag for detecting organophosphorus pesticides, carbamates nerve agents, and pesticides of leachate in contaminated groundwater [282–285]. Energy storage applications of bimetallic nanoparticles include CuS nanochips [286], sheet-like Cu–Co supercapacitor [287], Ag–Cu [288], and Co–Zn [289], respectively. Ni–Mo, Ag–TiO and Cu–Ag have also been used as nanocoating for mild steel protection against corrosion [290], the self-cleaning of tellurite zinc–silicate glass [291], and as conductive nano structure coating [292].

5.5. Bimetallic Application in Physics and Chemistry

In the field of chemistry and physics, bimetallic nanoparticles have been used for various applications including catalysis and optics (Table 4). Catalysis is the process of increasing the rate of a chemical reaction by adding a substance known as a catalyst that can increase the rate of reaction by lowering the activation energy of the reaction. This allows the reaction to occur at a faster rate, without the need for additional energy input. Bimetallic nanoparticles have been used for such application. A study reported the use of Mn–Cu catalytic agent for dye degradation [238]. The degradation activity was tested against methyl red, methyl orange and eriochrome black T. The result shows good degradation efficiency of bimetallic nanoparticles. Similarly, Ag–Pt catalysts were used for the hydrolysis of NaBH₄ [293]. Bimetallic nanoparticles were found to lower the activation energy and yield high hydrogen under low temperature which suggest that the bimetallic nanoparticle has a great potential for hydrogen storage application.

Table 4. Bimetallic application in physics and chemistry.

Types of BMNP	Light Source	Compound/Dosage	Degradation%/Activation Energy/Conversion Rate	Reference
Mn–Cu	visible light	240 µg/mL of methyl red	78.54 ± 0.16% degradation	[238]
		240 µg/mL of eriochrome black	87.67 ± 0.06% degradation	
		240 µg/mL of methyl orange decayed	69.79 ± 0.36% degradation	
Ag–Pt	–	–	25.61 kJ/mol activation energy	[293]
Pd–Pt	–	–	13.93 kJ/mol activation energy	[21]
Pd–Ag	–	NaBH ₄	27.01 kJ/mol activation energy	[61]
Pt–Cu	Sun light	Toluene conversion	55% conversion rate	[294]
Pd–Au	–	HDO of vanillin at room temp.	99% conversion rate	[295]
Au–Pd	–	Hydrodechlorination of aryl chlorides	95% conversion rate	[296]
Ag–Pd	–	Alcohol oxidation	up to 97% yield	[297]
Au–Pd,	–	Oxidation of glycerol	42.9% yield	[298]
Au–Pt	–	Oxidation of glycerol	29.4% yield	[298]
Au–Pd	–	H ₂ O ₂ production	99% yield	[299]
Au/Pd–TiO ₂	–	Alcohols oxidation to aldehydes	83.3% conversion rate	[300]

As for physical application, a Au–Cu bimetallic nanocrystal with orthorhombic morphology was successfully synthesized [301] and embedded in sodium borosilicate glass. The microstructural investigation of bimetallic nanoparticles suggested that Au–Cu intermetallic nanostructure was generated in the glass. Z-scan technique was applied at the wavelength of 800 nm to reveal the third-order nonlinear optical properties of the obtained glass. Similarly, bimetallic nanoparticles have been used as self-cleaning and

anti-reflective coatings on glass. $\text{TiO}_2\text{-SiO}_2$ was used to construct multifunctional antireflective coating [302]. $\text{TiO}_2\text{-SiO}_2$ coating presented an average transmittance of 97.7% and a maximum transmittance of 98.4% over the visible light and near infrared region of electromagnetic spectrum. It demonstrated very high photocatalytic activity, good hydrophilicity and favorable robustness which makes them extremely attractive for application in solar photovoltaic cells and lenses. A similar application of $\text{SiO}_2\text{-TiO}_2$ double layer for solar glass anti-reflective coating was also reported [303].

6. Challenges and Future Prospective

Bimetallic nanoparticles have gained significant attention in recent years due to their unique properties and many potential applications. Looking forward, there are many outlooks and future perspective of bimetallic nanoparticles. The development of new synthesis techniques can enhance the production of bimetallic nanoparticles with controlled morphology. This will give a provision for the tuning of activity and selectivity by enabling them to be used in a wider range of applications. Additionally, bimetallic nanoparticles have the potential to play a significant role in the development of sustainable and green technologies. They can be used as a catalyst for various environmental applications such as water treatment, energy conversion/storage and air pollution control. For instance, bimetallic nanoparticles have been studied as catalysts for the conversion of biomass to biofuels, which could contribute to the reduction of greenhouse gas emissions [304]. Subsequently, the use of bimetallic nanoparticles for biomedical application could enhance the efficiency and specificity of treatments while simultaneously reducing the side effects [305]. Likewise, integrating bimetallic nanoparticles with emerging technologies such as nanosensors and nanoelectronics can lead to the development of innovative and high-performance devices, although safety and the regulation of nanoparticles is an important parameter which needs to be considered for their future use. Since nanoparticles have shown an exponential application, there is no doubt that these particles will be released into the environment intentionally or unintentionally. The impact of the release of these nanoparticles is most likely unknown and remains a major concern, although a number of toxicity assessments of bimetallic nanoparticles using different cell/animal models have been carried out [235,306]. Thus, the toxicity of nanoparticles depends on the stabilizing agent, the dose used and the ionic charge at the surface to the nanoparticles. Further research is highly needed to determine the potential toxic effects of these nanoparticles and guidelines should be established for their use and disposal. Overall, the future outlook for bimetallic nanoparticles is promising, with potential applications in various fields and the development of advanced synthesis techniques and integration with emerging technologies. Continued research and collaboration between scientists, engineers and policymakers will be necessary to fully realize the potential of bimetallic nanoparticles in the future.

7. Conclusions

The field of nanotechnology has witnessed considerable advancement over the last decade. It has been applied in many areas, including biology, medicine, engineering, environment, physics and chemistry. This is because of the fascinating and synergistic effect between the two metals. This review comprehends the overview of bimetallic nanoparticles, types, synthesis, characterization, application and toxicity. However, there is still much work needed to be done to improve the biocompatibility of bimetallic nanoparticles because of their toxicity and potentially hazardous effects. In addition, the green synthesis approach is a promising method that can give rise to more biocompatible and less toxic bimetallic nanoparticles due to increasing environmental pollution.

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