A REVIEW ON SYNTHESIS OF COPPER-SILVER BIMETALLIC NANOPARTICLES

Sampat R. Shingda[1,2] , Sudip Mondal[2] , Kailas A. More [3] , Nilesh V. Gandhare [3]
*Pranali S. Hadole2
[1] Department of Chemistry, Arvindbabu Deshmukh Mahavidyalaya, Bharsingi Dist. Nagpur, Maharashtra, India
[2] Department of Chemistry, Seth Kesarimal Porwal College Kamptee Dist. Nagpur, Maharashtra, India
[3] Department of Chemistry, Nabira Mahavidyalaya, Katol Dist. Nagpur, Maharashtra, India
shingdasampat@gmail.com, kailasmore081988@gmail.com, sudipmondal5555@gmail.com
*Correspondence author: nilkanth81@gmail.com

Abstract

The study of Copper-Silver bimetallic nanoparticles (Cu-Ag BNPs) has grown significantly, especially in last decade. Cu-Ag BNPs has been synthesized by using biogenic, chemical, and physical methods. The biosynthesis of Cu-Ag BNPs mediated by plant extract is simple, low cost and safe for environment. Plant extract contains phenolic compounds like alkaloids, flavonoids, terpenoids, tannin etc. are act as reducing agent and stabilizing agent are ligand moieties like carbonyl, carboxyl and amino groups were useful for synthesis of BNPs and obtain non-toxic by-product. In chemical methods reducing agent like sodium borohydride, hydrazine hydrate, ascorbic acid etc. are used for the reduction of Ag(I) and Cu(II) into Ag(0) and Cu(0) respectively, and stabilizing agent like poly (vinyl pyrrolidone) (PVP), Poly (ethylene glycol) (PEG), Poly (vinyl alcohol) (PVA) etc. are prevents the further oxidation of silver and copper. Inphysical synthesis no requirements of reducing agent and stabilizing agent, simply deposition of one pure metal on another metal.To the best of our knowledge, there are no separately review papers in the literature on the synthesis of Cu-Ag BNPs by biological, chemical, and physical methods. Therefore, we provide a clear perspective on the synthesis of Cu-Ag BNPs.

Keywords: Biological synthesis, chemical synthesis, Cu-AgBNPs, nanoparticle synthesis, , physical synthesis,

Introduction

Bimetallic nanoparticles have gained attention in recently due to their favourable biological and industrial applications [1].Bimetallic Nanoparticle is combining of two different metal and having particle size is in between 1-100 nm. Bimetallic nanoparticles are currently the subject of interest in intense investigation and research is in progress due to great properties (catalytic, thermal optical, electrical and magnetic) compare with monometallic nanoparticles [2,3]. Synthesis methods of bimetallic nanoparticle are co-reduction, successive reduction method and electrochemical method [**Fig.1**]. In co-reduction method, two precursors and stabilizing agent added together in suitable solvent. Metals are presents in ionic form to convert into zerovalent required reducing agent into it. In successive reduction, first added one metal precursor with stabilizing agent followed by reducing agent after first metal reduce completely then add another metal into it, this method leads to formed core-shell bimetallic nanoparticles. In electrochemical method, bulk metal converts into metal atom. In this method, two anodes are made up from bulk metal and cathode is platinum metal plate, stabilizing agent mixed with electrolyte and current passed through ions and metals is formed at anode and reduced by platinum metal plates [4-7]. Bimetallic Nanoparticles are also synthesized by physical, chemical, and biological method, it involves Thermal and photochemical deposition, chemical vapour deposition, sputtering, sol-gel,

chemical precipitation, micro-emulsion, hydrothermal etc. Bimetallic nanoparticles can be found in form of alloy and intermetallic compound and having different structures like crown jewel, hollow, core-shell and alloy structure [3]. Bimetallic nanoparticle fabrication has drawn a lot of attention due to the numerous chances it offers to alter and improve its optical and electronic properties through engineering of the particle's composition, structure, and even geometric appearance. Many bimetallic nanoparticles, suchas AuCu, AgCu, RuCu,PdCu,PtCu,FeCu,NiCu,PdAu,PtPd,PdRu, PtCo and PtNietc. have been used as catalyst in aerobic oxidation the oxygen reduction reaction hydrogenation the Sonogashira reaction, oxidation of formic acid, degradation of organic contaminants hydrogenproduction, ethanol electro-oxidation, methanol electrooxidation and hydrogenolysis [8]. One of the objectives of this review is to study the synthesis of bimetallic Cu-Ag nanoparticles. These metals have very different reduction potentials, so the synthesis of mixed metal nanoparticles is quite difficult. However, by controlling the reaction sequence and reaction temperature, some control can be exerted and various nanoparticle microstructures and compositions have been obtained [9]. Individually, Cu and Ag monometallic nanoparticleshows lack of promising optical, catalytic, and structural properties compare to bimetallic nanoparticle. Therefore, combining the two metals (Cu: Ag) presents new opportunities for fine-tuning the resulting product's structure and morphology for desired applications [10]. In this present review we discussed about various methods for synthesis of Cu-Ag bimetallic nanoparticle, the metal precursors, reducing agents and stabilizing agents that used for respective nanoparticles. Synthesized Cu-Ag BNPs analysis discussed by different spectroscopic and microscopic techniques.

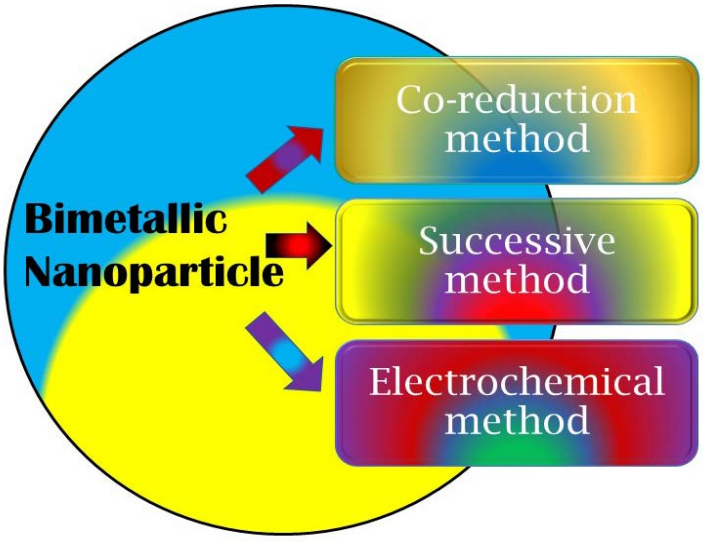

Fig.1: Methods of synthesis of Bimetallic Nanoparticle

Synthesis of Cu-Ag Bimetallic Nanoparticles:

In general, the NPs synthesis method includes two preparation processes: from top to bottom (by disassembling larger objects) and from the bottom to up (by reducing metal cations). The top-down approach begins with the bulk material and fragmentation by external mechanical forces in the presence or absence of catalysts. This method is performed by various techniques, such as evaporation-condensation, laser ablation, or other physical methods. Although this is a faster method, there is no control over the shape and size of BNPs. However, these procedures have several disadvantages, as they require the use of toxic chemicals, produce harmful by-products, and require high energy consumption. In addition, these processes are quite difficult to extend if industrial-scale manufacturing is required. The bottom-up approach begins at the atomic and molecular level, which is assemble the nanoscale level. This method is performed by various biological and chemical methods. In this method, the size and shape can be controlled by adjusting the synthesis parameters. This is a slower method [11-12].Therefore **Fig.2** Shows different Physical, Chemical and Biogenic methods of synthesis of Cu-Ag bimetallic nanoparticle.

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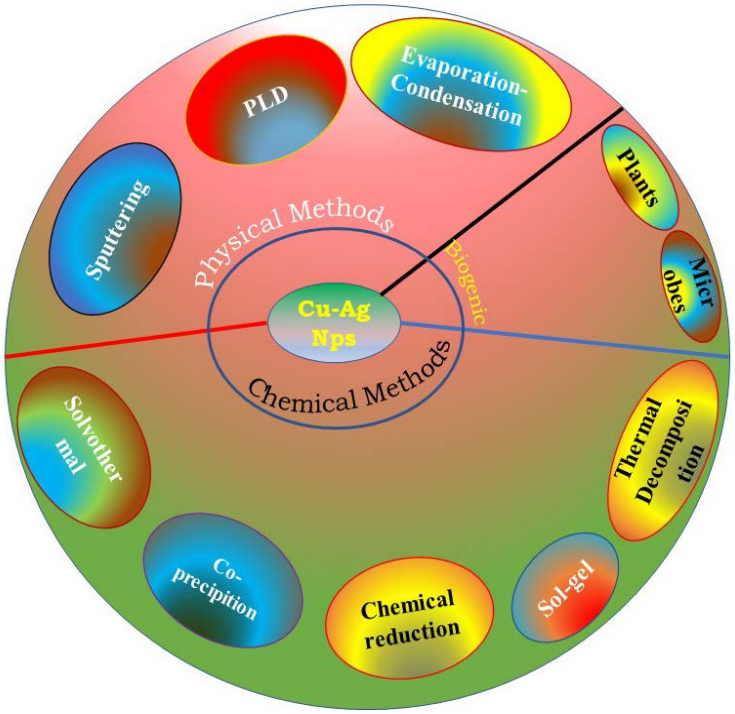

Fig.2: Synthesis of Cu-Ag bimetallic nanoparticle by various methods

Synthesis of Cu-Ag nanoparticle by Biological Method:

Previous studies have shown that different biological path-ways can be used to make nanoparticles using plants, bacteria, fungi, algae, and yeast, as they contain metabolites that can reduce metal salts and formulate nanoparticles. In addition, these substances do not only act as a reducing agent, as they are simultaneously involved in the stabilisation of nanostructures. Plants extracts contain phenolic compounds (flavonoids, terpenoids, tannins, and alkaloids) that act as reducing agents and stabilizing ligands moieties (carbonyl, carboxyl and amino groups). Another advantage of the biological synthesis route is the possibility of production on an industrial scale. To date, there is no known operation for the industrial manufacture of nanoparticles by these techniques. However, this would be beneficial as the main raw material is renewable. The process would require minimal energy, resulting in low operating costs and almost negligible toxicity of the waste [11].

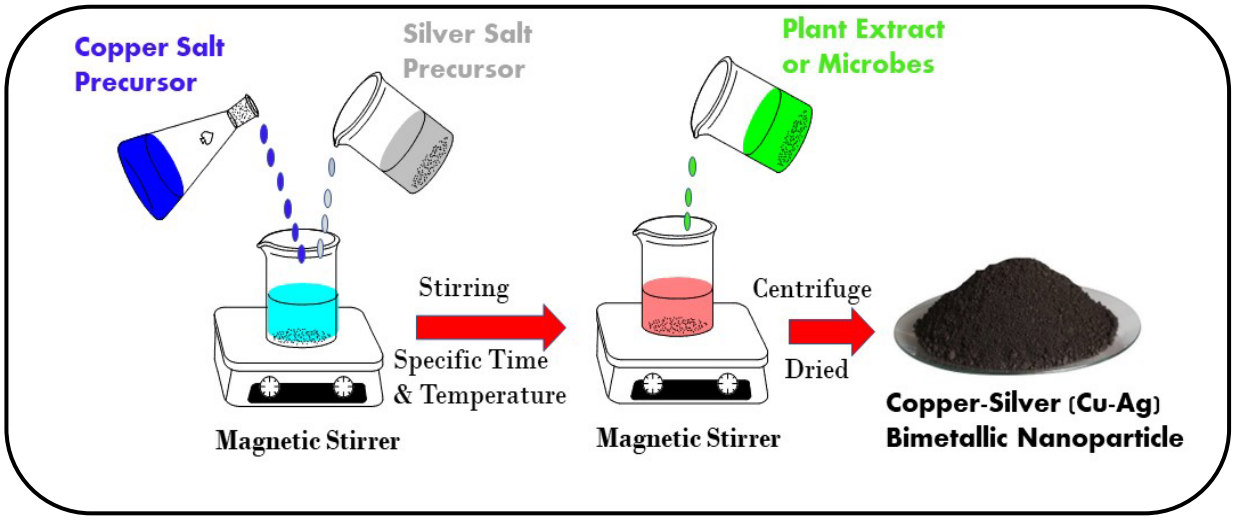

Figure-3: Schematic diagram of synthesis of Cu-Ag Bimetallic nanoparticle by Biological method

F. Ameen etal. reported synthesis of Cu-Ag bimetallic nanoparticle by using fungus *A. terreus*under microwave irradiation.In this synthesis process metal salts and fungus kept together in microwave for 15 min. they tested with two different powers i.e. 350W and 500W

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for same period time. They report optimum yield at 350 W power and size of particle is 20-30 nm in spherical shape [13]. H. R. Ghorbani and R. Rashidi et al. used bacteria suspension for Cu-Ag BMNPs. In this preparation,suspension of *R. capsulate* added to metal salt of copper and silver and reaction carried out for 30 min the colour changes from colourless to pink and then deep brown. They characterized the Cu-Ag BMNPs and get 4-15 nm in size and spherical shape [14].B. Biyela et al. had studied about synthesis of Cu-Ag BMNPs by using leaf extract of *K. Africana*. They combined extract with metal precursor's stirring for 6 hours at 100 °C and colour changes from light brown to dark brown and obtained 10-20 nm particle size and spherical in shape [15]. J. Al-Haddad et al. succeed in preparing bimetallic copper-silver nanoparticle using natural polyphenol extracted from the date palm leaves. They have taken equal volume copper and silver of specific molar concentration , mixed and heat at 95 °C for 10 min then add plant extract and keep for stirring about 1h, finally stored at room temperature. In this synthesis polyphenols present in the date palm leaves as an efficient reducing agent and Sidr leaves extract used as capping agent. They studied with three different molar concentration (i,e, 0.01M, 0.05M and 0.10M) and they get high yield at 0.01M concentration. Thus, the lowest bimetallic salt concentration of 0.01M was chosen for further studies. Elemental analysis of Cu-Ag confirmed by EDX analysis, from SEM analysis observed that the semi-spherical structure of copper-silver particles. Structure of Cu-Ag structure confirmed by XRD and get 26 nm particle size [16].

Rosbero et al. had reported biosynthesis of bimetallic silver/copper nanoparticles by using leaf extract of *Carica papaya*by co-reduction method.The synthesized nanoparticles observed unique star-like structure and particle size of ∼150 nm by using SEM and TEM analysis. XRD analysis revealed that the sample is crystalline (monoclinic phase) in nature with observed diffraction peaks corresponding to Ag, Ag_2O and CuO [17]. G. Mamatha et al. demonstrated three step process for developed antimicrobial cellulose nanocomposite films with in situ synthesized silver-copper bimetallic nanoparticles by using important medicinal plant *Vitex negundo* (Vavili) leaves, and which is acts as bio-reductant and stabilizing agent. The formation of Ag/Cu bimetallic nanoparticles were observed by the change of colour of cellulose films. XRD confirm that structure of Ag/Cu nanoparticles. The SEM and EDAX spectrum confirmed the presence of Ag/Cu elements and average size of Ag/Cu bimetallic nanoparticle is ∼60 nm [18]. O. Rocha-Rocha et al. have been obtained bimetallic Ag/Cu nanoparticles by green synthesis using *Opuntia ficus-indica* plant extract. The sample were analyzed by TEM, revealing core-shell nanoparticles with size of 10 nm to 20 nm with ellipsoidal shape[19]. D. Sharma et al. pointed out eco-friendly and cost-effective technique for the synthesis of *R. emodi* root extract-mediated copper-silver nanoparticles. Metal precursors and R. emodi root extract simultaneously added under continuous magnetic stirring for 3 h at 90 °C temperature. Formation of the bimetallic Ag-Cu NPs indicated by colour changes from light brown to black. Through the FTIR analysis, it can be confirmed that the hydroxy and phenolic compounds present in the *R. emodi* root extract. TEM analysis shows average particle size of Ag-Cu NPs in between 40 and 50 nm and spherical shape [20].

T. Dayakar et al. was successfully synthesized Ag@CuO core shell nanostructures using *Ocimumtenuiflorum* leaf extract. In this they prepared Ag@CuO by adding different concentration of copper precursor to silver solution and then plant extract add dropwise to it and maintained temperature 80 °C for 6 h. The characterization results shown spherical shape core shell and average particle size about 28-30 nm by SEM and HRTEM, elemental composition was confirmed by EDAX and chemical composition was confirmed by FTIR. Crystalline size d-spacing, dislocation density and strain were calculated by analysing XRD patterns [21].

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Table-1: Synthesis of Copper-Silver Bimetallic nanoparticles by biological method.

Synthetic Method	Metal Precursors	Plant Extract/ Microbes	Name	Particle size	Shape	Ref. No.
Microwave	Copper Nitrate & Silver Nitrate	Fungus	*Aspergillus terreus*	20-30 nm	Spherical	[13]
Co-precipitation	Copper Nitrate & Silver Nitrate	Bacteria	*R. Capsulata*	4-15 nm	Spherical	[14]
Co-precipitation	Copper Chloride & Silver Nitrate	Leaf extract	*K. africana*	10-20 nm	Spheres & rods	[15]
Co-precipitation	Copper Nitrate & Silver Nitrate	Leaves extract	*P. dactilifera* (Palm tree)&sidr	26 nm	Semi spherical	[16]
Co-reduction	Copper Nitrate & Silver Nitrate	Leaf extract	*Carica papaya*	∼90-150 nm	Star like	[17]
Co-precipitation	Copper sulphate & Silver Nitrate	Leaves extract	Vavili*(Vitex negundo)*	∼60 nm	Spherical	[18]
Co-precipitation	Copper Nitrate & Silver Nitrate	Leaves	Cactus *(Opuntia ficus-indica)*	10-20 nm	Ellipsoidal	[19]
Co-precipitation	Copper acetate & Silver Nitrate	Roots extract	*Rheum emodi*	40-50 nm	Pseudo-spherical	[20]
Co-reduction	Copper Nitrate & Silver Nitrate	Leaf extract	*Ocimumtenuiflorum*	28-30 nm	Spherical	[21]

Synthesis of Cu-Ag Bimetallic Nanoparticle by Chemical Methods:

Most common approach for synthesis of Cu-Ag bimetallic nanoparticle is chemical reduction by organic and inorganic reducing agents such as sodium citrate, ascorbic acid, sodium borohydride, Tollen reagents, N, N-dimethylformamide (DMF), Hydrazine hydrate, Oleylamine, and sodium hypophosphite are used for reduction of copper ions (Cu^{2+}) and silver ions (Ag^{+}) in aqueous or non-aqueous solutions. These reducing agents reduce Cu^{2+} and $Ag^{+}$and formed into metallic Cu^{0} and Ag^{0} respectively, which is followed by agglomeration into oligomeric clusters. These clusters lead to formation metallic colloidal copper and silver particle. It is important to use protective agent to stabilize dispersive nanoparticles during the synthesis of bimetallic nanoparticle, and protect the NPs that can be absorbed on or bind onto nanoparticle surfaces, avoiding their agglomeration. The stabilizing

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agents are used for synthesis of Cu-Ag BMNPs are Poly (vinyl alcohol) (PVA), Poly (vinylpyrrolidone) (PVP), Poly (ethylene glycol) (PEG), Dodecanethiol, Starch, HexadecylamineSodium citrate and Cysteine [22-23]. The different methods have been reported for synthesis of Cu-Ag bimetallic nanoparticle like Co-precipitation, sol-gel, hydrothermal, solvothermal, polyol reduction, thermal decomposition and microwave etc.

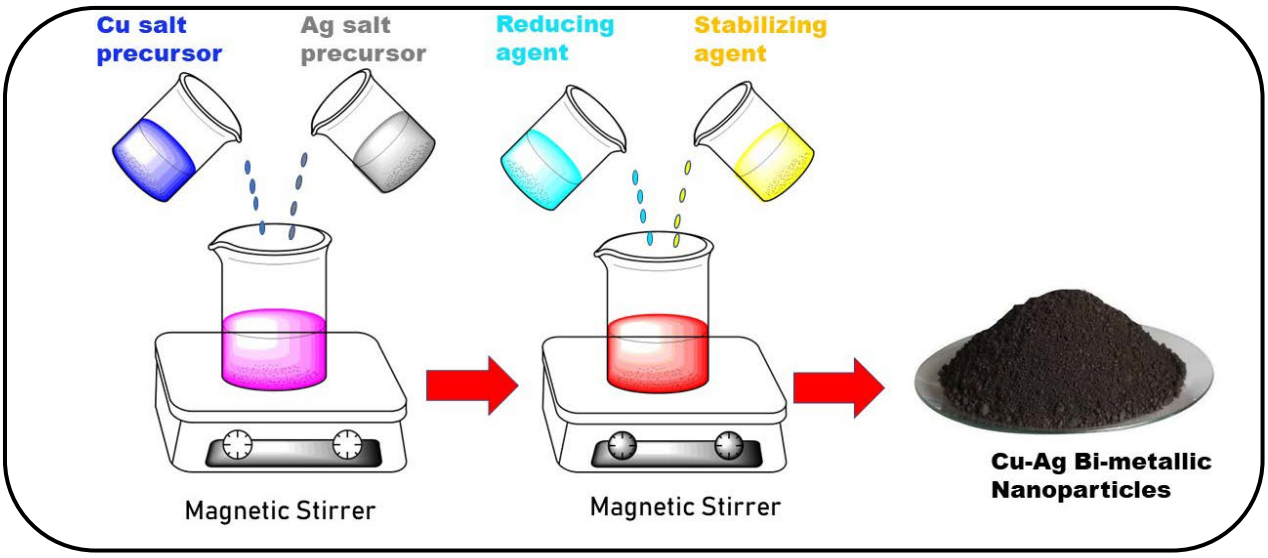

Figure-4: Synthesis of Cu-Ag BMNPs by chemical methods

S. Mureed et. al. reported synthesis of Cu:Ag bimetallic nanoparticles with various concentration ratios (2.5, 5, 7.5 and 10 wt%) of silver in fixed amount of copper were synthesized using co-precipitation method with ammonium hydroxide and deionized water as solvent, polyvinyl pyrrolidone as a capping agent and sodium borohydride and ascorbic acid as reducing agents. XRD patterns demonstrated well-crystalized product and FTIR analysis observed band position between 600 and 900 cm^{-1} shows formation of Cu:Ag bonding. From SEM images of synthesized Cu:Ag bimetallic nanoparticle, it was observed that small sized particles were deposited on the surface of large particles. TEM image showed particles seem like as dark and bright region and formation of core-shell structure. Formation of core-shell bimetallic NPs with different Cu:Ag ratios yielding irregular quasi-spherical NPs [24]. Z. Chen et al. reported Air-stable Cu-Ag bimetallic NPs have been synthesized at gram scale under a microwave-alcohol reduction process. The synthesis of Cu-Ag NPs was carried out according to a two-step procedure. Single Cu NPs were prepared in the first step and successive Ag deposition was carried out in the second step. The solid product exhibit high resistance against oxidation in air and no copper oxides are detected after storage of longer than six months in air or heating below 118 ^{o}C. XRD confirmed the structure of Cu-Ag and TEM observed core-shell structure with average particle size is 12-30 nm and spherical shape [25].J. Sopousek et al. demonstrated chemical solvothermal co-reduction method to obtained Ag-Cu bimetallic nanoparticle from metalloorganic precursors in a mixture of organic solvents. The molecular precursors were dissolved in oleylamine and this solution was injected into hot solvent composed of 1-octadecene and oleylamine at 230 ^{o} C. Ag-Cu formed solid with face centre cubic lattice and no oxides observed on the AgCu nanoparticle surface. By the DSC method, it was found that the AgCu nanoparticles do not show the melting point depression. The EDX microanalysis identifies an average metal composition of Ag-42wt% Cu. The TEM and SEM were used for morphology study and observed spherical shape and average particle size between 20-40nm [26].

M. Paszkiewicz et al. used chemical reduction method for synthesis of Ag/Cu bimetallic nanoparticles, for that they used silver citrate and copper acetate as metal precursors, water: isopropanol (3:1) as a solvent, PVP as a stabilizer and sodium borohydride as a reducing agent. Single-step reduction process has been used to obtain Ag/Cu alloy and from double-step reduction processobtain core-shell Ag/Cu

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nanoparticles.They prepared five types of bimetallic colloids (i.e. alloy Ag/Cu, Ag core/Cu shell, Cu core/Ag shell, NPs Cu/ions Ag^{+}, NPs Ag/ions $Cu^{2+)}$ and having different λ_{max}values i.e. 410 nm, 408 nm, 413 nm, 5o1 nm, 487 nm, 398 nm respectively. TEM analysis observed the average particle size in between 35 nm to 40 nm and morphology is close to spherical. The EDX spectra observed that the core of bimetallic NPs was rich in copper. However, the shell mostly contained silver. This spectrum clearly indicated that the silver content is higher than copper content in NPs core, while the shell of NPs region was rich in copper [27].N. R. Kim et al. reported thermal decomposition and galvanic displacement methods for synthesis of Ag-Cu bimetallic nanoparticles. In this preparation copper firstreduced usingoleylamine by heating to 220 ^{o} C for 2h while stirring, as indicated by the change in colour of the solution from cobalt blue to dark red then silver salt was added to coper nanoparticle further stirred at 180 ^{o} C for 6h.Ag-Cu nanoparticles characterized by XRD, TEM, EDS and observed uniform and spherical nanoparticles with a diameter of 13.9 nm. XPS measurement showed that the Cu atoms of Ag-Cu bimetallic nanoparticles were less oxidized than those in the Cu-only particles [28]. C. Lee. Demonstrated two-step process that consists of thermal decomposition and galvanic displacement methods for synthesis of uniform Ag-Cu core-shell nanoparticles. Nanoparticles was confirmed through characterization using TEM, XRD, EDS and investigated oxidation stability by XPS. They get smaller particle size about 13.5 nm with spherical shape [29]. M. Banik et al. pointed out simple method of synthesis of stable bimetallic copper-silver nanoparticle by successive reduction of copper nitrate and silver nitrate using hydrazine hydrate as reducing agent, gelatin and PVP as the capping agents. The spherical shaped particles were of core-shell structure with a core of Cu atom and surrounded by shell of Ag atoms. Average crystal size is calculated by the Scherrer's formula from XRD data was found around 23 nm, which was different from that determined by TEM due to imperfection crystallization. The EDX determined atomic proportion of Ag : Cu(0.8:1) in the NP was in consonance with the molar ratio (1:1) precursors of Ag and Cu for synthesis of Cu-Ag NPs. TEM spectra revealed round shaped structure and the average particle size was 100±10 nm [30]. T. Balkan et al. was succeeded in the synthesis of Cu-Ag alloy by one pot wet-chemical protocol. In this novel facile protocol, Oleylamine served as both reducing and reducing agent, Oleic acid acted as co-sufactant and octadecene was used as a solvent. In this they control the composition of Cu and Ag for synthesis of Cu-Ag NPs. In this study, besides the Cu40Ag60 NPs, two other compositions of CuAg alloy NPs containing less amount of Cu (C30Ag70) and higher amount of Cu (Cu60Ag40) were synthesized by using the Cu/Ag molar ratio of 3/4 and 3/2 respectively. TEM image observedboth having similar particles diameter in the range of 8-9 nm. XRD patterns of three different compositions of CuAg NPs show characteristic features of the fcc crystal structure [31].

M. Tsuji et al. demostrated two-step polyol reduction process for preparation of Cu@Ag Core-Shell nanoparticles. Formation of Cu@Ag nanoparticle is confirmed using energy-dispersed X-ray spectroscopic (EDS) measurements. The Cu particle oxidation was suppressed by Ag shell covering [32]. Q. Dou et al. had been synthesized Ag-Cu alloy in one pot by a thermal decomposition method using 1-octadecanol which is mild, non-toxic and cheaper reductant. tn this they prepared Ag-Cu alloy by varying molar ratio of Ag and Cu from 1:9 to 9:1. The better monodispersity and size uniformity observed by using TEM and EDS and revealed particle size in between 13-22nm and spherical shape [33].T. P. Ang et al. successfully synthesized Cu-Ag bimetallic nanoparticle by liquid phase method. In this they studied different molar ratio of Cu and Ag (i.e. 1:1,1:2, 1:3, 3:1, 0:1 and 1:0). From the spectroscopic and microscopic technique molar ratio of Cu:Ag (1:1) shows better properties. XRD and TEM observed average particle size was 4-6 nm and spherical shape [34]. Z. Chang et al. pointed out one step polyol reduction method for synthesis of Ag@Cu at different heating reaction time. During the preparation solution colour started to change from yellow, green, brown, black, copper and reddishbrown after heating for 4.5, 5, 7, 10, 15, 20 and 25 min respectively and these colour changes suggested that contribution of Cu increased with increase reaction time. In this process Ag^{+} was reduced

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fast than Cu^{2+}because reduction potential of Ag^{+}/Ag^{0} (+0.78 eV) higher than Cu^{2+}/Cu^{0} (+0.34 eV).TEM revealed that Ag-core Cu-shell (Ag@Cu) nanoparticles having spherical shape and average particle size is 180±20 nm. UV spectra observed bands for Ag and Cu were at 430 nm and 606 nm respectively [35]. J. Huang et al. demonstrated seed-mediated method for synthesis of Ag-Cu NPs with three different mass ratios of Cu to Ag i.e. Ag_1-$Cu_{0.4}$, Ag_1-$Cu_{1.1}$ andAg_1-$Cu_{3.2}$. The synthesized nanoparticle is confirmed by UV, XRD, XPS, EDS, FESEM, TEM etc. and found spherical shape and 25-30 nm particle size. They observed that, Ag_1-$Cu_{1.1}$ shows excellentcompared to another molar molarratio [36]. H. Jiang et al. have been prepared Ag-Cu alloy nanoparticles by polyol process by varying the molar ratios of Ag to Cu with 1:1, 1:2 and 1:3. They observed that UV spectra of Ag and Cu peak shows at 431 and 592 nm respectively, but Ag-Cu alloys peak observed at 534 nm.From TEM image analyzed particle size around 50-80 nm and semi spherical shape [37].Yi-Shien Lee et al.reported chemical reduction method for the synthesis of Ag-Cu nanoparticle, for this synthesis concentration of silver kept fixed and concentration of copper was varied. Synthesized Ag-Cu confirmed using XRD, EDX etc. and TEM analysis revealed particle size is 20-40 nm [38]. S. Mureed et al. developed Cu:Ag bimetallic nanoparticles with various concentration ratio (2.5, 5.0, 7.5 and 10 wt%) of Ag and fixed amount of Cu. XRD confirmed phase purity and distinct fcc structure. FTIR confirmed the presence of vibrational mode of Cu:Ag BNPs and UV-visible spectroscopy revealed reduction in band gap with increasing Ag content. SEM and TEM revealed spherical morphology of Ag dopped Cu bimetallic nanoparticle [39].S. Shang et al. demonstrated two step synthetic method for preparation of copper-silver (Cu@Ag) core-shell bimetallic particle were Ag coated over Cu [40]. M. Singh et al. study reveals the formation of Ag-Cu solid solution through chemical reduction of silver and copper salts, hydrazine hydrate as reducing agent and PVP as stabilizing agent. They found particle size is about 100 nm to 200 nm [41].M. Singh investigates the co-reduction of silver nitrate and copper nitrate in aqueous medium using hydrazine hydrate and starch as reducing agents. XRD analysis reveals maximum solid solubilities in Ag and Cu, with hexagonal Ag-2H phase. LSPR spectra show absorbance maxima for Ag-rich and Cu-rich alloy nanoparticles, with smaller aggregates having Ag-rich compositions [42].M. Taner et al. synthesized Ag-Cu nanoalloys through co-reduction with hydrazine hydrate, exhibit superior antibacterial behavior against Escherichia coli strains, demonstrating better antibacterial properties compared to Ag-only nanoparticles [43].C. Tsai et al. studied the structural evolution and oxidation of Cu@Ag core–shell nanoparticle deposits upon heating in air were investigated quantitatively via in situ synchrotron radiation X-ray diffraction. They found particle size about 25 nm [44].M. Valodkar et al. prepared metallic and bimetallic nanoparticles of copper and silver using microwave assisted chemical reduction in aqueous medium. Starch was used as a stabilizing agent, and ascorbic acid was used as a reducing agent. The nanoparticles showed surface plasmon absorption resonance maxima at 416 and 584 nm, and antibacterial activity at micromolar concentrations [45].L. Wang et al. synthesized Ag-Cu nanoalloys through chemical reduction method, with a small, uniform, and spherical morphology. The size distribution mainly focuses on 80nm-90nm, with an average composition of $Ag_{48.9}$-$Cu_{51.1}$. The optical absorption spectrum confirms the formation of Ag-Cu nanoalloys [46].W. Wu demonstrated one pot synthesis of Cu/Ag alloy NPs using glucose as reducing agent. They examined their catalytic activity on reduction of 4-nitrophenol and Cu/Ag NPs shows excellent catalytic activity [47]. X. Yu et al. synthesized uniform, anti-oxidative Cu-Ag core-shell nanoparticles with an average diameter of 50 nm. The nanoparticles' morphology and structure are studied using various techniques. Conductive inks are prepared by mixing them with ethylene glycol and ethanol. A sintering mechanism is proposed, showing improved performance at lower temperatures [48]. Y. Yuan et al. proposed one-step synthesis method for formation of copper and silver core-shell nanostructures. This environmentally friendly fabrication simplifies copper particle surface treatment. The study investigates thermal stability and electrical properties of Cu@Ag core-shell nanoparticles, revealing high

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spherical degree and low sheet resistance after annealing at high temperatures [49].J. Zhao et al. synthesized superfine bimetallic Cu-Ag core-shell powders using copper sulfate pentahydrate and silver nitrate, ascorbic acid, and cyclodextrins. The Ag/Cu ratio significantly influenced the coatings' uniformity and antioxidation. The surface composition analysis showed only small parts of Cu atoms were oxidized. The hindrance of cyclodextrins played a crucial role in forming these powders [50].

Table-2: Synthesized Cu-Ag BMNPs by Chemical Methods

Synthetic Method	Metal Precursors	Reducing agent	Stabilizing agent	Particle size	Shape	Ref. No.
Co-precipitation	Copper Chloride and Silver Nitrate	Sodium Borohydride ($NaBH_4$)	Polyvinyl pyrrolidone (PVP)	-	Quasi-spherical	24
Microwave alcohol reduction	Copper myristate and Silver myristate	-	-	12-30 nm	Spherical	25
Solvothermal co-reduction	Copper acetylacetonate and Silver acetate	Oleylamine and Octadecene	Oleylamine and Octadecene	20-40 nm	Spherical	26
Chemical Reduction	Copper acetate and Silver citrate	Sodium Borohydride ($NaBH_4$)	Polyvinyl pyrrolidone (PVP)	35-40 nm	Spherical	27
Thermal Decomposition	Copper acetylacetonate and Silver Nitrate	Oleylamine	Oleylamine	13.9 nm	Spherical	28
Thermal Decomposition	Copper acetylacetonate and Silver Nitrate	Oleylamine	Oleylamine	13.5 nm	Spherical	29
Successive reduction	Copper nitrate and Silver nitrate	Hydrazine hydrate	Gelatin & PVP	100±10 nm	Spherical	30
Solvothermal	Copper acetylacetonate and Silver acetate	Oleylamine	Oleylamine& Oleic acid	8-9 nm	Spherical	31
Two-step polyol reduction	Copper acetate and Silver nitrate	Ethylene Glycol	PVP	80 nm	Spherical	32
Thermal Decomposition	Copper (II) acetate and Silver acetate	1-octadecanol	Oleylamine& Oleic acid	13-22 nm	Spherical	33
Liquid-phase method	Copper nitrate and Silver nitrate	Sodium borohydride	1-dodecanethiol	∼4-6 nm	Spherical	34
Polyol reduction	Cupric acetate and Silver nitrate	Ethylene Glycol	PVP	180±20 nm	Spherical	35

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Seeded-growth colloidal method (nucleation)	Copper acetate and Silver nitrate	Ascorbic acid	Hexadecylamine	20-30 nm	Spherical	36
Polyol reduction	Copper (II) acetate and Silver nitrate	Ethylene Glycol	PVP	50-8- nm	Semi-spherical	37
Chemical reduction	Copper nitrate and Silver nitrate	Dextrose	PVP	20-40 nm	-	38
Co-precipitation method	Copper (II) chloride and Silver nitrate	Ascorbic acid and sodium borohydride	PVP	-	Spherical	39
Two step synthesis method	Copper sulfate pentahydrate and Silver nitrate	Sodium hypophosphite monohydrate	PVP	80±5 nm	-	40
Chemical reduction	Copper nitrate and Silver nitrate	Hydrazine hydrate	PVP	100-200 nm	-	41
Co-reduction method	Copper nitrate and Silver nitrate	Hydrazine hydrate	Starch	56-59 nm	Spherical	42
Chemical reduction method	Copper (II) acetate and Silver nitrate	Hydrazine hydrate	Sodium citrate and cysteine	-	-	43
Chemical reduction method	Copper (II) chloride and Silver nitrate	Trisodium citrate dehydrate	PVP	25±2.7 nm	-	44
Microwave	Copper nitrate and Silver nitrate	Ascorbic acid	Starch	20±5 nm	Spherical	45
Chemical reduction method	Copper (II) acetate and Silver nitrate	Sodium borohydride	PVP	60-130 nm	Spherical	46
Chemical reduction method	Copper (II) chloride and Silver nitrate	Glucose	Hexadecylamine	85 nm	Spherical	47
Polyol reduction	Copper sulfate pentahydrate and Silver nitrate	Sodium hypophosphite monohydrate	PVP	50 nm	Spherical	48
Wet chemical method	Copper sulfate pentahydrate and Silver nitrate	Glucose and Ascorbic acid	PVP	100-300 nm	Spherical	49
Chemical reduction method	Copper sulfate pentahydrate and Silver nitrate	Ascorbic acid	cyclodextrins	100-150 nm	Spherical	50

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Synthesis of Cu-Ag Bimetallic Nanoparticle by Physical Methods:

Evaporation-condensation, sputtering and laser ablation are most important physical methods are used for synthesis of nanoparticles. In chemical process there is chances of contamination due to solvent and other chemicals are used but in case of physical method not contamination of solvent in the prepared thin films and the uniformity of nanoparticles distribution [23].

G. Radnoczi et al. had been prepared nanoparticles using Direct Current (DC) magnetron co-deposition of Ag and Cu on thin carbon film in Ar atmosphere of 0.2 Pa pressure. The deposited quantity of Cu/Ag is about 1 nm thickness. During the process, two sputtering targets consisted of 99.99 % pure cu and Ag. The sputtering speed ranged between 0.1 and 1nm/s and was controlled by sputtering power of the targets. Phase separation occurs above 5nm particle diameters in the 15 and 30 at % Ag composition range. TEM analysis without further purification reveals 2-10 nm average particle size at different composition of Ag and spherical in shape [51].K. Chen et al. fabricated Cu-Ag core-shell particles using silver sulphate and tartaric acid as a reducing and chelating agent. The molar ratios of TA and Ag significantly influenced Ag coatings on Cu particles. They found 50 to 150 nm and uniform spherical shape. The composite particles showed satisfactory antibacterial properties against Staphylococcus aureus and Escherichia coli [52].S. Lee et al. prepared Ag-Cu_2O nanoparticle using electrochemical deposition method. They observed phase separate Ag-Cu_2O and phase blended Ag-Cu_2O in solvent NH_3 and KCN respectively. In electrodeposition method, deposition of metal ions can be kinetically control using different solvents. Particle size of synthesized material is around 50 nm [53].M. Liang et al. prepared Cu@Ag nanoparticles with various morphologies using the galvanic exchange method, evaluated for thermal stability, and investigated as conductive ink. The optical properties were simulated using finite-element methods [54].

Q. Jia et al. developed a supersaturated Ag-7.3wt%Cu alloy nanoparticle film using pulsed laser deposition. The nanoparticles can conduct bonding in air without a reduction agent, with a shear strength above the die shear standard. The bonding process at 250-400°C was accompanied by Cu separating behaviour, with neck formation delayed due to Ag-Cu alloy's thin oxide shell [55].

Table-3: Synthesized Cu-Ag BMNPs by Physical Methods

Synthetic Method	Metal Precursors	Reducing agent	Stabilizing agent	Particle size	Shape	Ref. No.
Sputtering	Pure Cu and Ag metal	-	-	2-10 nm	Spherical	[51]
Sputtering	Copper powder and Silver sulphate	Tartaric acid	Tartaric acid	1-1.5 µm	Spherical	[52]
Electrochemical co-deposition	Copper sulphate and Silver nitrate	Lactic acid	NH_3& KCN	∼50 nm	-	[53]
Galvanic exchange method	Copper (II) acetate and Silver nitrate	Oleylamine	-	100 nm	Non-regular shape	[54]
Pulse laser deposion (PLD)	Pure Cu and Ag	-	-	44-172 nm	-	[55]

Discussion:

Reduction potential of Ag is higher than Cu therefore silver is reduced easily at low temperature. During synthesis of Cu-Ag BMNPs when increase heating temperature the rate of Cu reduction increase, so microwave heating method would be advantageous for synthesizing nanoparticle core-shell structures using metals with very different redox potentials. The biosynthesis of Cu-Ag BMNPs is simple, low-cost, and safe for environment over chemical and physical method.

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Conclusion:

This review has highlighted the methods of synthesis and characterization of Cu-Ag BMNPs. In this review mostly strong reducing agent such as sodium borohydride, hydrazine hydrate, ascorbic acid etc are used and Poly-vinyl pyrrolidone (PVP), Oleylamine are use as excellent stabilizers are used for synthesis of Cu-Ag BMNPs.

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