An Overview of Strategic Non-Biological Approaches for The Synthesis of Cupper Nanoparticles

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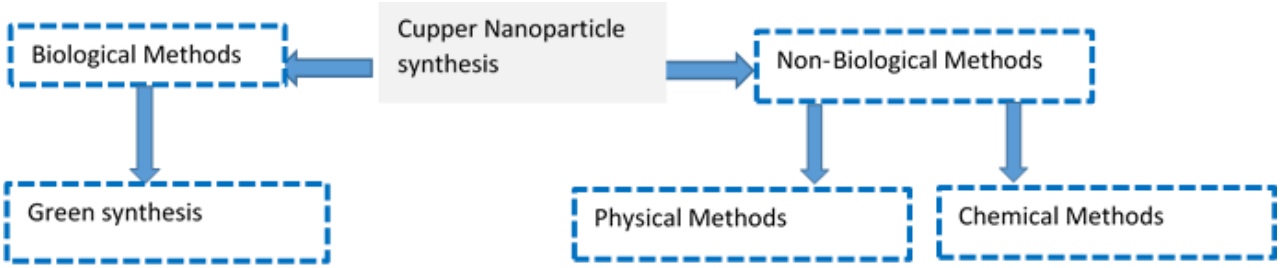
DOI: 10.2478/acmy-2021-0005

Abstract:
Metal Nanoparticles show specific physical and chemical properties attributed to its small size and high surface area to volume ratio. These chemical and physical properties using different strategies and conditions enhance its biological application especially in the field of medicine. Earth abundant and cheap cupper metal is the essential element in many processes and has been used as a focus element to synthesize nanoparticles by different methods using new technology, which are being broadly classified as biological methods that includes green synthesis, microorganism etc. and the non-biological synthesis which includes chemical and Physical methods. Thus, the imperative need to synthesize cupper nanomaterial that are economic and efficient is necessary. This review have briefly described the modern methods to synthesize nanoparticles particularly focusing on the non-biological methods of cupper nanoparticles. An overview of current methodologies that are used for cupper nanoparticle mainly chemical reduction using organic and inorganic solvents, Reverse micelle, microemulsion, polyol method and several physical methods such as vapor condensation, photo irradiation and plasma synthesis methods are discussed.

Graphical Abstract:



Keywords: Cupper, Nanoparticle, Chemical Method, Metal Nanoparticle, Non-Biological Methods, Physical method

1.0. Introduction:

Nanotechnology (NT) is an advance and progressing field with wide variety of applications. The nanoscience deal with the nanoparticles of size 1-100nm.This small particle display tremendous activities. Not only has the size of the particle but the shape, structure and surface morphology of the nanoparticle had a huge impact on its biological activities [1]. Some of the application of nanoparticles include in the field of medicine, cosmetics, agriculture, material science, electronics, catalysis, pollution sensing, water purification, surgery, drug delivery, textile, food packaging, tissue engineering, sports, environment, electrochemical sensor, Waste water degradation, Ceramics [2-14]. Because of the ongoing growth in the field of NT it has attracted the scientists to develop novel and potent nanoparticle that may carry tremendous application which can be exploited for utilization according to the future demands. Of all of the different types of nanoparticles available including metallic nanoparticles, nonmetallic nanoparticles, metal oxide nanoparticles, polymer nanoparticles, core shell nanoparticles, nanoparticles that are of huge interest nowadays is the metallic nanoparticles [15-18]. It is attributed because of its small size and high surface area due to large surface area to volume ratio it can be effectively used against ever growing crafty bacteria and antibiotics [19]. It has gain interest among scientists because of its antibacterial, antimicrobial, anti-inflammatory and anticancer, immunosuppressant properties [20-30].

Copper nanoparticle has wide variety of applications but the one particularly interesting is its use as ink in electronic printing. Development of thermally stable and conductive ink was achieved by fabrication of copper nanoink where its resistivity as an electrode was successfully achieved for its potential application in industry [31,32]. Using modified pol method CuNPs were synthesized and then were utilized for its application in inkjet printer electronics. This method involved using ether-based solvent as a carrier solution to be deposited on various substrates. These deposited materials are then converted into conductive copper ink at low temperature reductive sintering process. CuNPs were synthesized by vigorously mixing sodium hypophosphite ethylene glycol and heating at 90oC. Copper sulfate solution in ethylene glycol was added to PVP/sodium hypophosphite solution. The solution changes color from green to heena indicating the formation of CuNPs. The reaction was then quenched, and CuNPs were separated, washed, centrifuged and vacuumed. These NPs were then weighed to the known amount and dispersed in ethanol, centrifuged, transferring supernatant to another container and drying the sediment in oven. Dispersion yield was determined by taking the initial cupper weight and that of sediment weight. The copper nanoparticles that remained dispersed in the ethanol supernatant were isolated and then used for ink production [33].

It has also been used as a catalyst where fabrication of CuNPs thin-films on indium tin oxide electrode has significantly increased its stability as well as catalytic activity for the reduction of nitrite and NO [34]. It is used as a catalyst by reducing CO2 by cuprous oxide derived cupper nanoparticle [35]. Carbohydrates are electrochemically detected using CuNPs [36]. Recently a sensor is constructed to detect the glucose level without an enzyme this sensor contain cupper nanocluster deposited on the film of a Nafion-solubilized multiwall carbon nanotube (CNTs)-modified glassy carbon electrode (CNTs–GCE), which fabricated a Cu–CNTs composite sensor (Cu–CNTs–GCE) to detect glucose with nonenzyme [37]. Due to its vast applications in different fields from electronics to pharmaceutics cupper nanoparticles are synthesized by a number of methods. Copper Nanoparticles are also synthesized by using L-ascorbic acid. CuCl2.2H2O solution was reduced by L-Ascorbic acid by dropwise addition. The color change indicated the formation of NPs [38].

This review is an effort to support the already documented data of other researchers [39-41]. There are some good reviews that can be found on a similar topic where some researchers focused on cupper nanoparticle synthesis using chemical treatment option with summarizing its application in the field of catalysis or used as a filler in metal-metal bonding [42,43]. Supported metal nanoparticles with particular focus on CuNP and its application on its catalytic performance is described in great detail [44]. Optical properties of CuNP and its synthesis via chemical process are often explored by scientists due to the presence of surface plasmon resonance in the visible range make it use as an effective solar cell [45]. Some approached more towards the biomedicinal side

of research and focused more on the biological activies particularly antimicrobial agent or an anticancer agent [46,47]. The environmental aspect in relation to the effect of CuNP and its toxicity on fish and marine environment is discussed [48]. Despite of the extensive review articles available on different application and a particular methodology of CuNP synthesis, less effort is done to summarize all the basic processes of chemical and physical synthesis of CuNP.

This review will broadly classify and refer to the recent literature in order to give an overview of the different methods that can be used for the synthesis of CuNP. Synthesis of CuNP is by variety of biological and non-biological methods (physical and chemical methods) Figure 1. Nowadays a less expensive and environmentally friendly approach known as biological synthesis of nanoparticle using plant extract as reducing agent is widely used. However, all these technique to synthesis NPS is widely classified into two categories as top down and bottom up technique. The former technique involved chemical and physical process that reduces the size of particle produced, the latter approach involved the synthesis of nanoparticle and then its assembly in to the final product.

2.0. Biological and Non-Biological Methods for the synthesis of Cupper Nanoparticles

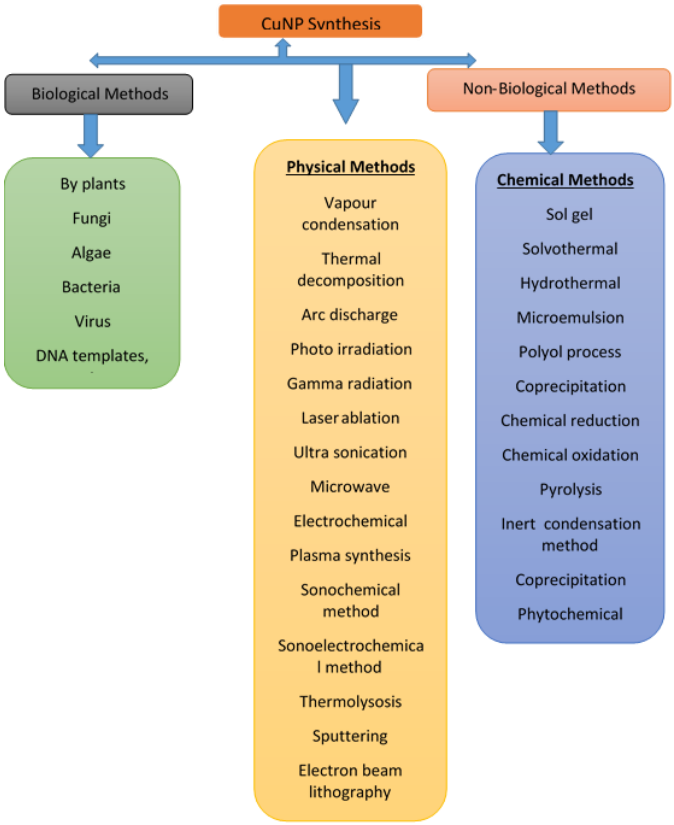


Figure 1: Biological and non-biological method of cupper nanoparticle synthesis

2.1. Biological Methods

Biological method report the synthesis either by microorganism like yeast or fungi or by plant extract. For instance, the biological synthesis of CuNPs was achieved using aqueous solution of CuSO4.5H2O which was reduced by leaf extract of Magnolia Kobus. Leaves were dried out at room temperature, washed, sterile and boiled. Leave broth was added to CuSO4.5H2O for the purpose of reduction. The solution changed color indicating the formation of CuNPs as confirmed by UV visible spectroscopy with maximum absorbance at 560nm. Its spherical appearance was confirmed by TEM. Different factors were varied to determine its relation with particle size and the result suggested that increasing the concentration of leaf broth upto 15% decreased the particle size to an appreciable amount. However, the reverse was observed as the particle size showed a decrease with increasing CuSO4 solution. Besides concentration, temperature has also effect on particle size and biological activity. Antibacterial activity of formed nanoparticle was tested against gram negative Ecoli (ATCC 25922). Latex foam was added to CuSO4 and leaf broth solution which was then kept at shaking incubator. Bacterial cells were grown and cultured in LB and agar medium respectively. Microbe's colony were counted against control. Latex foam were dipped in cupper sulphate solution which changed color with increasing concentration of cupper nanoparticles. As the average size decreased the antibacterial properties started to increase. Moreover the CuNPs synthesized using plant extract had more potent antibacterial activity as compare to the one prepared by using sodium borohydride and Tween 20 [28,49]. Syzygium aromaticum bud extract, Azadirachta indica leaves extract or bacterium such as Shewanella loihica PV-4 or by fungi such as Stereum hirsutum has also been used to synthesize CuNP [50-53]. The reduction by the plant extract lies in the biomolecules that are present in the plant that help to reduce the metal ion in one step. These biomolecules are basic secondary metabolites like terpenes, flavonoids, phenolic compounds, alkaloids etc [54].

2.2. Non-Biological Methods

The non-biological method has also been extensively utilized to synthesize CuNPs.

2.3. Chemical Methods

2.3.1. Chemical reduction method

There are several organic and inorganic reductant's used for the synthesis of CuNP, while the range of surfactants is also large. However, there are some less common reagents that can also be used as reducing agents. One report suggests using inorganic reductant vanadium sulfate salt as a reducing agent while (PVP) and sodium dodecyl sulphate (SDS) as two stabilizers for the CuNP synthesis. The reaction occurred at fast rate, low temperature and te nanoparticles were formed with less chances of agglomeration [55]. CTAB can also be used as a reducing agent for the synthesis of CuNP which display antifungal activities [56]. There has been several reports suggesting using NaBH4 as a reducing agent [57]. For instance a facile one pot synthesis of uniform

monodispersed CuNP of size in range of 40–80 nm can be obtained by using sodium borohydride as a reducing agent and starch as a stabilizing agent. The process involve the formation of cupper ammonia complex followed by addition of HCl until the solution neutralizes. NaBH4 and starch are dropwise added at room temperature until the solution changes color to dark brown which indicated the formation of cupper nanoparticle [58]. Using Polyethylene glycol (PEG) as a capping and ascorbing acid as a protecting agent while keeping the typical reductant NaBH4 is used synthesize CuNP where chemical reduction of CuSO4 salt occur in water without inert gas protection. Another report synthesizing CuNP without inert gas protection is by Dung Dang "et al" where CuNP of 10nm was synthesized using ascorbing acid as a protecting and PEG as a capping agent where Sodium borohydride was used as a reducing agent [59].

There has been one report using water as a solvent and keeping the typical reducing agent like NaBH4 to synthesize CuNP [60]. Besides sodium KBH4 can also be used as a reducing agent for synthesis of CuNP [61]. Samim "et al" synthesized CuNP using NaBH4 as a reducing agent and sodium citrate as capping agent. The particle size was controlled with varying concentration of reactant and capping agent [62]. Bambo "et al" used a modified version of this procedure where Instead of sodium citrate organoclay was used as a stabilizing as well as a substrate for nanoparticle formation. Cupper sulfate solution in the presence of organoclay was reduced with NaBH4 to form organoclay/Cu nanoparticles [63]. A novel method has been proposed to synthesize CuNP at low temperature , weak ascorbic acid is used to reduce cupper sulphate in aqueous solution. These nanoparticles were starch-protected zero-valent copper (Cu) nanoparticles [64]. Fallahzada "et al" synthesized CuNP of 7 - 58 nm at room temperature using Na2HPO4 as a reductant PVP and PVA as surfactant to reduce CuSO4 in aqueous media. Solution was centrifuged and dried to obtain the desired product [65]. PVA was added to aqueous cupper salt solution and stirred for 10 min. hydrazine hydrate (HH) and sodium formaldehyde sulfoxylate (SFS) was added and again stirred for 30 min which gave brown color solution which was dried in vacuum. Absorption of the band at 600nm indicated the presence of cupper nanoparticle formation [66]. Another process that involved reduction of cupper salt involved Graphite powder which is oxidized to graphite oxide which was then latter used to produce reduced grapheme oxide. The process involved by putting H2SO4 to powdered graphite and then allowing it to cool with circulator at 20C,accompanied by addition of KMnO4 with constant stirring.

Temperature is elevated to 40C and the solution was heated at this temperature for 1 hour. Followed by addition of distill water which further increases the temperature to 100C. Addition of H2O2 to the mixture which was diluted with distill water. The mixture was purified and washed to obtain grapheme oxide (GO). This GO was then reduced to black powder. For the purpose of synthesis of CuNPs NaOH solution was drop wise added to CuSO4.5H2O Temperature of the solution was raised and sediments obtained are filtered. Glucose and distill water is added until the appearance of dark red solution. Aqueous solution of glycine and sodium borohydrine added drop wise to the mixture to obtain Cu+2:NaOH:Glycine:NaBH4 .Reduced graphene oxide/copper nanoparticles (rGO/Cu NPs) composite was then prepared from this mixture which was utilized as a hetrogenous catalyst [67]. Chen "et al" synthesized Graphene-Copper Nanoparticle Composite of average size of 20.8nm by in Situ Chemical Reduction using potassium borohydride as a reducting agent. GO powder was dispersed in double distilled water which was sonicated for 1 hour. A solution of CuSO4 and EDTA was prepared and added to GO powder solution which was again sonicated for further 10min. A solution of KOH and KBH4 were added to the micture which was stirred and heated to obtain black brown color Graphene cupper nanoparticle composite. The synthesized nancomposite was then used for Electrochemical Sensing of Carbohydrates Facile [68]. The following table 1 illustrates some of the CuNPs synthesized using chemical reduction approach.

Table 1: CuNP Synthesis by Simple Chemical Reduction

Type of NP	Reducing agent	Characterization	Shape of NP	Size of NP	Application	Refs
CuNP	NaBH4	HRTEM, XRD, BET surface area analysis, , XPS	Spherical (HRTEM)	HRTEM (10–150 nm, average diameter of 61 nm)	Water treatment	[69]
Chitosan loaded CuNP	NaBH4	UV-Vis , FESEM, EDX, XRD, TGA	N/A	SEM (80-90 nm),	Toxic dye reduction	[70]
CuNP	C6H8O6	UV/Vis, TEM, XRD	Spherical	TEM (39.9 nm)	Catalyst for p-Nitrophenol Reduction	[71]
Chitosan nanocomposite fibers supported CuNP	NaBH4	FE-SEM, Oxford-EDS, XRD, FTIR, Cyclic voltammetry	N/A	Fityk software (11.93 nm),	Catalyst for 4-nitrophenol (4-NP)	[72]
CuNPs supported into mesoporous films, functionalized with COOH and NH2	NaBH4	UV-vis, TEM, HR-TEM, EELS, XPS,	Spherical	TEM(SiO2–COOH-Cu10 ~3.8 nm, SiO2–NH2-Cu10 ~3.5 nm)	Catalytic activity	[73]
CuNP	NaBH4	UV-vis, TEM, FTIR,	Shape depends on concentration of PEG	PEG:CuNP (w 6 : 1 (14-50nm), 7 : 1 (9-29nm), 9 : 1 (4-6nm)	Optical Property	[59]
Graphene-copper nanoparticle composite	KBH4	SEM, XRD, FTIR, cyclic voltammetry, CE capillary electrophoresis	N/A	XRD (Pure Cu Cu 15.4nm Cu in composite (20.8 nm)	Electrochemical Sensing of Carbohydrates	[68]
starch-protected zero-valent copper (Cu) nanoparticles	C6H8O6	XRD, SEM, EDX,	cubic	XRD(28.73 nm)	N/A	[64]
CuNP	H6N2O	UV-Vis, DLS, NTA, SEM, XPS,		DLS (average diameter 50 nm), SEM (50-70 nm)	Antimicrobial	[74]
Nanofluids consisting CuNP	N2H4	SEM, EDS	Spherical, square	SEM (50–100 nm)	Thermal Conductivity	[75]

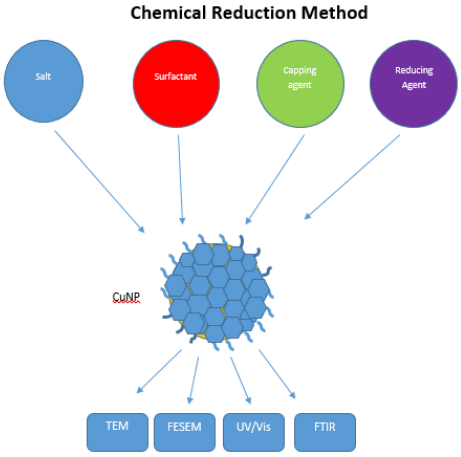


Figure 2: Chemical reduction method

2.4. Reverse micelle

There are several reports suggesting using reverse micelles for the synthesis, one such example is of using Compressed Liquid and Supercritical Fluid Reverse Micelle Systems. In this system water is used as solvent. This system also comprises of surfactant. The role of the surfactant is to create those micelles which are stable thermodynamically. These micelles are comprising of poles of water which are nanosized. The ratio of water to surfactant is significantly related to size of the micelles. While the size of copper nanoparticles is not dependent on the above stated ratio by using AOT as surfactant. Cu-(AOT)2 absorbed on micelles of AOT and its reaction is performed in propane, a compressed solvent, isooctane as a cosolvent , hydrazine as a reducing and ethane as a supercritical liquid, resulted in the reduction of Cu-(AOT)2 and production of cupper nanoparticles [76]. This synthesis and size of the particle is effected by thermophysical factors such as pressure and temperature of compressed and supercritical solvents [77]. Another group of scientists synthesized a controllable size CuNPs using a modified reverse micelle method where cupper acetate was used which reacted with L-ascorbic acid in a solution containing water and xylene in the presence of oleic acid and oleylamine as surfactants [78].

2.5. Microemulsion

Microemulsion particularly using water in oil microemulsion for the synthesis of nanoparticles has been extensively used in the past however using supercritical fluid/water emulsion has been of main focus nowadays as it promises controlled synthesis of nanoparticle [76]. One such example of using a microemulsion system involved the use of CO2 as a supercritical fluid and Sodium cyanoborohydride and N,N,N¢,N¢-tetramethyl-p-phenylenediamine as a reducing agents. These nanoparticles were synthesized in AOT reverse micelle, compressed propane and supercritical ethane. perfluoropolyether phosphate as a co surfactant allowing the soluibilty of CO2 in microemulsion. Appearance of light red color indicated the formation of CuNPs which was observed using insitu spectroscopy [79]. Non-ionic water and oil microemulsion system was used to synthesize CuNPs where aqueous cupper chloride was reduced by NaBH4. The system also contained Triton X-100 (TX-100) , n-hexanol, cyclohexane. TEM displayed a particle size of 5-15nm with particles being well dispersed and fomed within the water droplets [80].

2.6. Polyol method

A pol method involving non- aqueous solvent as a reaction medium in air is has also been used to synthesize Mono disperse CuNPs. This method allowed to design particle of control size with minimum surface oxidation. Poly (N-vinylpyrrolidone), diethyleneglycol and Sodium phosphinate monohydrate is used as capping agent, reaction medium and reducing agent respectively. The reducing agent undergoes oxidation reaction in aqueous medium to release electron which are then used to reduce cupper ion. By increasing the concentration of reducing agent the particle size of the formed nanoparticle decreases. The decrease in the particle size is led by the decrease in the temperature of the reaction. While increase in the injection rate also leads to the decrease in particles size. This synthesis method resulted in the synthesis of the 45 nm monodispersed copper nanoparticles [81].

2.7. Solvothermal Method

Solvothermal method provides an efficient inexpensive and size-controlled synthesis of nanoparticles. Therefore, a facile and novel method has been introduced to synthesize CuO nanoparticle using alcohothermal process where copper acetate is used as a starting material. Stable nanoparticle of size 3-9nm were successfully obtained [82]. Nanostructures of semiconductors like Copper indium sulfide (CuInS2) and sphere-like kesterite Cu2ZnSnS4 (CZTS) nanoparticles can also be successfully synthesized by solvothermal method [83,84]. Synthesis of such nanoparticles will have a promising application in the field of photovoltaic devices and other electronics. CuInSe2 is a leading material for high-efficiency and radiation-hard solar cell applications [84].

2.8. Hydrothermal method

Cu based nanoparticles are extensively synthesized using hydrothermal method. For instance Cu nanowires are synthesized with increased electrical conductivity using Cu-glycerol complex and surfactant sodium dodecyl benzenesulfonate assisted by hydrothermal reduction process [85]. Cu@Cu2Ocore-shell microspheres composite can also be synthesized using interfacial hydrothermal process GuO “et al” synthesized high quantum yield fluorescent CuNP using one step hydrothermal method [86]. In this process sodium citrate NH4HCO3 and water were first placed in Teflon and then drying oven, followed by hydrothermal treatment at 180 _C for 4 h. Floresecne CuNPs were obtained by cooling and purification [87].

2.9. Sol-gel methods

Sol-gel method is employed quite often for synthesis of nanosize catalytic materials. Sol gel method was used for the copper loaded titinia nanoparticles. In this method titanium butoxide was used. It was hydrolyzed slowly by addition of exact stoichiometric amount of water. Solution also contained glacial acetic acid and anhydrous butanols as regents. CuCl2 was added during stirring and at the mark of 8 hours transparent solution was obtained which was dried in furnace. Powdered form of titanium supported cupper nanoparticle Cu/TiO2 was obtained by crushing the desired sample [88]. Using

poly(sulfopropylmethacrylate) (p(SPM) as a hydrogel for the insitu synthesis of CuNP by redox polymerizations using NBH4 as a reducing agent. The prepared NP can be used for reduction and removal of nitrophenols from wastewater [89].

2.10. Physical Methods

2.10.1. Photochemical methods

Photochemical method has several advantages over frequently used chemical reduction method of synthesis of CuNP. Firstly it avoids the undesirable by product that can be obtained by using the reducing agent in chemical reduction method. Proper wavelength will be selected to control the rate of reaction. the reaction will be carried out at room temperature. CuNP was synthesized by photoreduction using PVP surfactant with varying concentration and intensity of light. At 254nm and a concentration of 0.2– 0.1 M of smaller than 4nm was obtained [90].

2.10.2. UV irradiation

Cu metal absorb light in the visible region and display optical properties. Cu metal nanoparticles are synthesized by photochemical method where metal ions are reduced to metal by light radiation. A group of scientists used the same procedure by reducing aqueous solution of CuSO4 by UV irridaition from Hg lamp using benzophenone (BP) as a photo-sensitizer and poly(N-vinylpyrrolidone) as a stabilizer. The formed nanoparticles were very stable and had an average particle size of 15nm [91]. The methods usually employed for the synthesis of cupper nanoparticle invlve the use of expensive salt. The approach towards less expensive and facile synthesis of CuNP using common cupper salt CuCl2 was carried out by Zhu"et al". CuCl2 being an insoluble intermediate was converted to copper–amine coordination compound and it is done by adding diethanol amine to an ethanolic solution of CuCl2 [92]. The formed mixture also contained a photointiator 184 and a capping agent PVP which is then photo reduced by UV radiation. UV–vis spectrophotometer showed absoption of band confiring the formation of CuNP. Nazar "et al" synthesized CuNP using radical photoinitiator and a copper-amine coordination compound, where PVP,pyrrole and Sodium ascorbate were used as capping and antioxidant agents. Copper compound was reduced to CuNP by UV irradiation [93]. Zhu "et al" synthesized CuNP by irradiation of UV upon cupper amine coordination compound. The solution also contained photointiator which upon decomposition produce free radicals. Complex compound is rapidaly reduced to cupper particle. Poly(vinylpyrrolidone) is used as a capping agent to prevent agglomeration of formed nanoparticles [92]. Giuffrida "et al" studied the effect of poly (vinyl pyrrolidone) (PVP) on CuNP formation by UV irradiation. Ethanalic solution of Cu (acac)2 was irradiated using UV. Light was absorbed by the solution at 254nm. Cu(acac)2 was first photoreduced to cupper (I) and then cupper alkoxide(I) which upon photosensitized reduction formed colloidal cupper. Precipetate appeared indicated the formation of NP. Addition of PVP stabilized the synthesized NPs and had the ability to control the size of NP [90].

2.10.3. Gamma γ - Irradiation reduction method

Pure cupper nanoparticles can be synthesized using gamma rays irradiation reduction method where gamma rays are used as a source of reducing agent, alcohol as radical scavenging agent and a stabilizer such as EDTA. The dose rate of gamma radiation is controlled by changing the distance between radiation source and that of solution. Gamma radiation produce hydroxyl radical into the solution which causes oxidation of generated cupper nanoparticle hence oxidizing radical scavenger such as DEG which acts as a capping ligand for the nanoparticles can also used. An anionic surfactant such as sodium dodecyl sulphate (SDS) is also used. Cupper salt such as cupper sulphate or cupper acetate. Hydoxy hydrogen and surfactant radical along with hydrated electron is produced by gamma radiation which causes reduction of Cu ion and production of Cupper nanoparticle. From spectroscopic analysis it was found that the addition of DEG increases the Cu peak intensity, suppreses the production of Cupper oxide nanoparticles and increases the production of pure cupper nanoparticle. DEG reacts with hydroxyl radical and converts into reducing agent which increases the reduction rate and hence the production of small particles with no large particles in solution. CuO and CuO2 are also produced along with Cu nanoparticles of small size with gamma irradiation however the oxide cupper NPS can be controlled by using DEG [94]. Another group of scientists synthesized copper-PAA nanocomposites using polymer polyacrylic acid in the presence of alcohol and EDTA stabilizer. Various methods have been employed to control the size of NPs which has the tendency to nucleate and agglomerate at nanoscale. One such method involve the use of large polymer molecules. Co60 is a source of gamma radiation which produces ionization upon contact with aqueous solution of cupper used. Stabalizers form covalent linkage with the nanoparticles to give it stability. Polymer like polyacrylic acid has a high crosslinking capacity which makes it an efficient encapsulating agent controlling the growth of cupper nanoparticle. Increasing polymer concentration increased the plasmon resonance. EDTA Ligands complexed with copper ions act as bridges for electron transfer from solvent to copper ions, favoring nucleation thus formation of smaller nanoparticles [95].

Ahmad "et al" synthesized cupper nanoparticles using gamma radiation in a dose dependent manner where the dose and dose rate was varied to study its effect on yield of synthesized nanoparticles. The process involved copper sulphate solution, ethanol scavenging agent, nitrogen and five different dose rates. A standard solution of CuSO4.5H2O was prepared with small amount of alcohol. Oxygen was removed from this solution by bubbling of nitrogen. The resulting solution was transferred into special tubes and was irradiated with gamma rays at different dose rates and absorbed doses. Irradiated samples were washed, centrifuged and the supernatant was analyzed using UV /Vis spectroscopy. Powdered sample was dissolved back in nitric acid and diluted to achieve the desired effective range for cupper solution detection. atomic absorption. Spectroscopy was used to determine the concentration of the dissolved sample. Washed and Centrifuged sample was dried with nitrogen flow at 60Co for XRD analysis which indicated the formation of cupper nanoparticles with presence of Cu2O in the sample. Spherical shaped particles of 2-10nm were confirmed by TEM. It was concluded that the yield of the copper nanoparticles produced from gamma irradiation did not influence by dose rate but depend on total absorbed dose [96]. Using Polymeric support of PVA film CuNPs were synthesized inside the polymer matrix by high dose dosimeter using gamma radiation. The characterized sample displayed post irradiation stability [97].

2.10.4. Microwave irradiation

A novel method has been proposed for the synthesis of well dispersed cupper nanoparticle where hydrazine is used as a reducing agent to reduce cupper sulphate solution in ethylene glycol in the presence of protective polymer under microwave irradiation. Ethylene glycol and CuSO4·5H2O were mixed with NaOH and N2H4·H2O. The obtained solution was placed in a microwave oven and irradiated for different intervals of 30s, 60s and 90s. It was again irradiated for another 2 min after boiling at 196C to keep it boiling. After cooling to room temperature, Cu nanoparticles were obtained by centrifuging and washing with ethanol several times [98]. Zhu "et al" prepared cupper nanoparticles using NaH2PO2. H2O as a reducing agent to reduce Cupper sulphate pentahydrate by irradiation with microwaves in the presence of the ethylene glycol. PVP and solution of Ethylene glycol-CuSO4 .5H2O was mixed. Then solution of the ethylene glycol-NaH2PO2.H2O was poured to it with constant stirring for 15 min. Then the mixture was vigorasly stirred for 5 min and was put in microwave. Color of the solution turned black so it was cooled to room temperature to get copper nanoparticles [99].

In polyol methods occur at close system which makes it a low temperature process. During this process polyol itself acts as a stabilizer as well as a solvent which prevent cogulation of large particles, hence size controlled synthesis is achieved. This method has been extensively used to synthesize metal and metal oxide nanoparticles. Reactivity of the reaction during this process is mainly effected by the temperature. Besides reactivity there are other factors like diffusion, formation and breaking of chemical bond and reduction potential of ethylene glycol. These factors favour microwave-heating techniques for

the fabrication of metal. A novel microwave-induced polyol route to synthesize Cu, Cu2O,CuO nanoparticles. Cu (OAc)2·H2O and EG were placed in microwave reflux system under ambient condition for 15 min. Colored Precipitates were formation as the reaction progressed , which were cooled centrifuged washed and dried at room temperature. The Suspension was characterized. Cu nanoparticle were formed at 197C and 100% EG to water solution [100]. A modified polyol method using Copper acetate hydrate (CuAc2.2H2O), Tween 80 (polyoxyethylene- (80)-sorbitan monooleate) was used as a stabilizing agent. CuAc2.2H2O was added to ethylene glycol and Tween 80. The resulting mixture was refluxed and stirred until the reduction of metal salt. The solution was allowed to cool and the CuNPs precipitate were obtained and removed by centrifugation. The NPs were then washed, dried and characterized [101].

2.10.5. Pulsed laser ablation

It is a physical, flexible vapor deposition technique where intense layer beam is focused on target material which converts it into plasma fume to be deposited on substrate. The process in liquid can be used for nanostructure generation and controlled fabrication of nanomaterials [102]. Using laser ablation in water stable colloidal cupper nanoparticle of size 30nm is synthesized while by changing the carrier medium to acetone the particle size also decreased to 3nm [103]. Surrounding liquid environment had effect on optical properties, size and stability of the molecule [104]. CuNP and its oxide has been synthesized by Swarnkar et al using pulsed laser ablation in water [105]. 1064 nm wavelength of 35 mJ/pulse energy was irriadiated on sample containing cupper and water for 30min, the resulting synthesized and aged colloidal NP of 6 days was characterized which showed spherical shaped 2-7 nm NP.The aging process converted CuNP to Cu and Cu2O nanostructure with self-assembly into cactus-like structure [106].

2.11. Electrochemical methods

Electrochemical methods encompass all those analytical techniques that measure the analyte potential or current in an electrochemical cell. There are different types of electrochemical methods. Some of the methods used to synthesize cupper nanoparticles are given below:

2.11.1. Electrochemical deposition method

Electrochemical deposition is an electrochemical method in which a thin and tightly adherent desired coating of metal, oxide, or salt can be deposited onto the surface of a conductor substrate by simple electrolysis of a solution containing the desired metal ion or its chemical complex [107]. Cupper nanoparticle containing diamond like film (Cu-DLC) has been synthesized using electrochemical deposition method. DLC films have limited practical application due to high internal stress and inadequate adherence to substrate however this can be improved by doping metallic element into DLC films. Copper-doped diamond-like carbon films could be obtained using acetonitrile solution of as electrolyte however the low rate of deposition of carbon causes codeposition of carbon and cupper. Therefore, the recent attempt was choosing Dimethyl sulfoxide (DMSO) as carbon source, acetonitrile as doping source to synthesize Cu-DLC under lower potential. The electrolytic cell comprised of negative electrode silicon and a positive electrode graphite where [Cu (CH3CN)4]ClO4/CH3CN and DMSO was used as electrolyte source and acetonitrile solution, [Cu(CH3CN)4]ClO4 as dopant. 150 V and 70oC bath temperature was used to deposit the film. During this deposition process cupper salt solution was added drop wise to the reactor. After deposition the sample was cleaned by acetone and then dried by nitrogen gas blowing.

Different spectroscopic techniques were used to study the composition, morphology and structure of synthesized film. Results revealed that Cu-DLC deposited on silicon substrate, the copper element was embedded in the amorphous carbon film and the codeposition rate of carbon film and copper cluster was relatively high [108]. Hashemipour “et al” synthesized CuNP using electrochemical deposition method. In the beginning of the experiment Cupper was reduced at cathode at low potential and then there occurred an increase of cathodic current which is attributed to copper crystallization. NP of averaging 20nm size was separated from electrode as a spongy layer. Size of nanoparticle was controlled with electrolyte concentration and current density [109]. Cupper carbonate NPs were synthesized using Taguchi robust design. Steel sheet cathode and Cupper anode were immersed in sodium carbonate solution across which an adjustable programmed voltage was applied. Upon the completion of the reaction, solid product were collected by centrifugation which was then repeatedly washed, dried. CuONPs were synthesized by thermally decomposing the finest carbonate nanoparticles prepared in a furnace at 350 °C for 120 minutes, in an air atmosphere. The synthesized NPs were spectroscopically analyzed and subjected to photocatalyst and degradation efficiency was calculated using formula. CuO nanoparticles were prepared through calcinating optimally prepared CuCO3 nanoparticles [110].

2.11.2. Sonoelectrochemical method

Industrial synthesis of metallic nanoparticle requires the use of electrolyte of high concentration which raise the problem of coagulation, aggregation and sedimentation thus limiting its use in fields that require stable dispersion of these NPs. In electrochemistry-controlled size NPs can be achieved by adjusting the current density or the applied potential. Highly dispersed NPs can be obtained using pulse sonochemical method. This process synthesizes shape and size-controlled synthesis with altering electric and sonic pulses. Hass “et al” synthesized well dispersed CuNPs using sonochemical method. The synthesized NP was stabilized by using non-ionic surfactant PVP poly(N-vinylpyrrolidone). Sonoelectrochemical device was used for the experiment which would produce a sonic pulse followed by electric pulse, titanium horn acted as cathode and an ultrasound emitter. Reaction occurred in an electrochemical cell where cathode was separated from anode by a sintered glass. Cupper deposition occurred within the cell, where the precipitate formed was washed and vacuumed dried. Addition of PVP polymer stabilized the colloidal suspension of cupper. XRD revealed the synthesis of pure dispersion CuNP.

Oxygen and nitrogen groups of polyvinyl skeleton forms a complex compound with cupper Cu2+-PVP by donating its lone pair electrons. This cupper in its complex form is reduced from +2 to 0 state on PVP polymer when an electric pulse is passed through it thus preventing the agglomeration of the metallic nanoparticle. TEM images showed that spherical and monodispersed cupper nanoparticle particles of 25-60nm are obtained. Controlling different parameters esp. current density control the size of nanoparticle [111]. Cupper nanoparticles stabilized in its solution as well as dried form, were synthesized in one phase system using alkanethiolate protecting monolayer. In solution form these particles showed quantized capacitance while in solid form under thermal annealing at low temperature, it formed different morphological structures like diamond, hexagon etc. This was in contrast to the previous reports which suggested the spherical nanoparticle formation upon thermal annealing. The synthesis process involved the dissolution of Copper (II) nitrate in nanopure water and addition of THF upon stirring. Dropwise addition of superhydride in this solution resulted in n-hexanethiolate-protected Cu nanoparticles formation. Toluene phase was separated, collected and dried. Free Tetraoctylammonium bromide and thiol were removed by washing the solid with excess methanol and acetone. Washing followed by filteration resulted in purified hydrophobic C6Cu particles. Long thermal anneling of these particles resulted in different geometric shapes [112]. Electrochemical deposition method has also been used to synthesize the fabrication of polymer assisted cylindrical poly- and single-crystalline cupper nanowire [113].

2.11.3. Sonochemical Method

Surfactant Mediated synthesis of elongated cupper nanoparticles are done using sonochemical method. The common problem arise during this type of synthesis is the agglomeration and change of particle morophology when high intensity UV radiation used. This problem was resolved by the synthesis

process copper hydrazine carboxylate (CHC) precursor and surfactant CTAPTS in an aqueous solution is ultrasonically reduced to red powder. Metallic CuNP coated with surfactant on its surface is formed which is confirmed by different characterization techniques [114].

2.11.4. Mechanical Milling

It is simple, low cost, high yield obtaining top down approach for the synthesis of nanomaterial and nanocomposite (Table 2). There are various types of milling devices depending on grinding of balls such as wet or dry ball milling, or on the basis of operation such as batch milling and continuous milling, on the basis of type of discharging material into tubular and flowing type ball mill [115, 116]. The most commonly used, however, is the high energy ball mill which includes tumbler ball mills, vibratory mills, planetary mills, and attritor mills [117]. The process involves the reduction of particle size when the ball, the grinding medium, falls on the top of particle from top of cylinder [118,119]. In high energy ball milling, the ball mill is subjected to high-energy collision from the balls. It is most commonly used for mechinal alloying of materials with non-equilbrium structures [120,121]. A series of nickel–copper alloy magnetic nanoparticles were synthesized by the use of mechanical milling of a mixture of nickel and copper powders. Different composition of both alloy were ball milled using steel vial under nitrogen atmosphere for 20 hours as further milling had no effect on X-ray diffraction of powdered blend. NaCl was added during the milling process to prevent agglomeration. Xray diffraction revealed the formation of Cu-Ni nanoparticle of 11nm. As the nitrogen content increased the curie temperature increased with it [122]. Yadav et al synthesized 21nm (at 40 hrs) CuNP by wet milling, planetary ball milling method. The process involved using two different sizes of balls (5nm and 3nm). Rectified Toulene was used as a wet medium where the milling speed was kept at 250 rpm. The particles were characterized by XRD, SEM, Nano Zetasizer [123].

Table 2: Synthesis of nanocomposite using different techniques

Type of Nanocomposite	Type of Mechanical Milling	Characterization	Ref
TiC-Graphene/Cu hybrid	Ball milling	XRD, TEM, SEM	[124]
Cu-NPs and GN/Al	Intermittent ball milling	SEM, TEM, XRD, XPS, Electron backscattered diffraction (EBSD) analysis	[125]
Cu-GNS	planetary milling	XRD, SEM, EDXS	[126]
Cu-SiC	high energy-planetary ball mill	TEM, SEM, XRD	[127]

2.11.5. Electrochemical Milling Method (ECM)

Metal NPs are fabricated by build up or bottom down method. Former involve chemical and physical processes that reduces the metal ion in solution or in solid state to form nanoparticle, the latter involve the mechanical grinding or mechanical milling to breakdown the bulk metal to nanolevel [128]. Synthesis of copper nanoparticles can be could be carried out in high yield by novel reduction process of ECM. Particle size and morphology can be controlled by controlling the current density. In this process the CuO and Li counter electrodes are used for the fabrication of the electrochemical cell. Copper was used as a base for electrode, poly- (vinylidene fluoride) (PVDF) as a binder while as separator the membrane of the microporous polypropylene was used. Cells were discharged and recovered powder were washed, separated and analyzed spectroscopically. The CuO electrode is redued by the electrical energy in the first discharge process. Formation of the nanoparticles of copper and copper oxide occur through Li electrode during discharge step. The XRD has confirmed the synthesis of the Cu, Li2O and CuO as final products of the discharge step. HCl and NMP were used for washing of the discharge copper oxide electrode from the impurities. After washing the pure CuO powder were obtained. To investigate the effect of the density of the current on the structure of the nanoparticle's different density of current wee applied to the electrodes. It was observed that the current density has significant effect on the size and morphology pf the nanoparticles [129].

2.12. Solid-Liquid Phase arc Discharge Process (SLPAD)

Selective synthesis of Cu nanoparticle can be achieved by SLPAD method. High purity cupper filaments were used as electrode. One of the electrodes was dipped in NaNO3 solution where the end other electrode was momentarily brought in contact with NaNO3 solution.AC was applied across the electrodes. An instantaneous current was generated between the two electrodes and arc discharge sparks was formed at the point end of the electrode that was momentarily brought in contact. The arc discharge process generates a large amount of heat which causes the copper electrode to be dissolved into solution. Moreover, the formed Cu clusters will form CuO colloidal solution upon oxidation. Ascorbic acid and hydrazine were mixed with starting solution for the synthesis of nanoparticles of copper and its oxide. After cooling the solution, the precipitates of the copper and its oxides were obtained which were washed with ethanol and water [130]. Cupper nanowire and nanorods can be synthesized using vacuum vapor deposition method This novel one-step procedure involves copper vapor generation and redeposition on a substrate under very low pressure or vacuum conditions [131].

2.13. Pulsed wire discharge method (PWD)

This is one of the energy efficient method for the synthesis of nanoparticle where a pulsed current is used to evaporate solid thin wire, the vapours so formed are then cooled in the ambient gas to form the nanoparticles. There has been few reports of using liquid medium, deionized water in PWD [132]. Coating of nanoparticles is usually done to hyberdize or passivate the nanoparticles [133]. Murai "et al" used the same approach by synthesizing the cupper nanoparticle by pulsed discharged method and successfully coating it with organic matter. It was also found that coating did not change the structure of the molecule but decreases the mean diameter as it prevents agglomeration [134]. Keeping an ambient pressure cupper nanosize powder of 10-100nm has been synthesized. There is also a direct relationship between the mean diameter of nanoparticle and ambient pressure [135]. Cho "et al" synthesized CuNP of 100nm diameter by PWD method. Submicron sized particle present in the nanoparticle powder has been investigated and is found to be attributed to liquid droplets due to lower energy deposition in the wire than vaporization energy of the whole wire. It was also found that energy deposition and current has a direct relation [136]. Suwa "et al" synthesized Ni–Cu nanopowders of <100nm by wire discharge method [137]. Electrical DC arc-discharge method was used to synthesize a 99nm CuNP by applying 275 V current in deionized water. Two same metals were used as electrodes which created plasma upon electrical discharge. A colloidal solution along with color change was observed. Sunlight illumination revealed a red color solution for CuNP. Ascorbic acid was added as reducing agent while polyvinyl alcohol (PVA) acted as capping agent. The obtained NPs were analyzed by UV, TEM and DLS. 578 nm surface plasmon resonance polycrystalline arrangement of highly dispersed NPs of various size and shapes were observed. TEM reported 86 nm while the Gaussian fitted data suggested a NP of size 99nm. The synthesized NP has an application in polymer solar cell [138].

2.14. Arc-Submerged Nanoparticle Synthesis System (SANSS)

Metal nanoparticle is also synthesized by innovative method called Arc-Submerged Nanoparticle Synthesis System (SANSS). In this method pure metal such as cupper acts as an electrode submerged in deionized water. When electrical energy is passed through electrode it produces submerged arc at very high temperature, which vaporizes the cupper metal electrode in the arc region. The metal aerosol and deionized water are both at temperature and pressure

which makes their volume expand. Water is evaporated to remove vaporized aerosol. When the metal aerosol moves through the non-vaporized deionized water, it can be immediately quenched and then solidified without excessive particle growth. Therefore, the vaporized metal aerosol is nucleated and grown into nano-scale particles. Result was copper nano crystalline particles with well controlled size [139]. Another group of scientists using the SANSS method successfully synthesized Suspended copper oxide nanoparticles of particle size 49.1nm [140].

2.15. Exploding wire method

A method in which rising current applied to thin electrically conductive wire vaporizes the wire and an electric arc over that vapor creates a shockwave and explosion. It is a well-known method used for the synthesis for metal nanoparticles method. Cupper nanoparticle is synthesized by this method while varying the ambient pressures to determine its effect on the nanoparticle. It was found that the mean diameter decreases with decrease in pressure [141].

2.16. Thermal Decomposition

Metallic Nanoparticles like cupper nanoparticles are synthesized at high temperature in the presence of organic surfactant like phenyl ether and oleic acid. The nanoparticles formed are oxide free, size controlled and highly crystalline with enhanced antibacterial properties against multidrug resistant bacterial strains. Synthesis process involves dissolving cupper chloride and sodium oleate in a mixture of hexane, ethanol, and distilled water. Heating under relflux for 4 hours and then solution is extracted by discarding the aqueous layer and washing the organic phase with distill water. Solution is concentrated by evaporating the liquid in the petri dish. The solid copper-oleate complex obtained is mixed with oleic acid and phenyl ether at room temperature. The obtained solution is heated during which brown color will appear indicating the formation of CuNPS [142]. A more modified procedure is used by masoud "et al" where thermal decomposition used for the synthesis of monodispersed size and shape-controlled cupper and CuO2 from precursor copper salicylidiminate in oleylamine. For this method sample was prepared by heating a mixture of cupper complex and C18H37N at 130C. Sample changed color to gray in the presence of nitrogen.

The solution was kept at 130C for 45 min and then heated to 230 C upon which it turned into red color solution, giving it a further 1 hour at same temperature, the solution is allowed to cool, precipitate and redispersed in C2H5OH and C6H12 respectively. purple/darkred solution appeared indicating the formation of CuNPs, which upon exposure to oxygen turns into blue color indicating Cu2O nanoparticle formation [143]. Kim "et al" used Cu-oleate complex as a precursor whose thermal decomposition produce monodispersed spherical copper nanoparticles at 0.05 M oleate concentration. CuCl2 reacted with sodium oleate in an aqueous solution to form Cu-oleate complex. Here Sodium oleate not only acts as a stabilizer of the synthesized NP but also as protector against oxidation [144]. Son "et al" synthesized uniform Cu2O coated Cu nanoparticles by thermal decomposition of copper acetylacetonate. Complex and that of oleylamine were heated to 230C and was kept at this temperature for 6 hours, producing a red-colored colloidal solution. The nanoparticles formed were oxidized to Cu2O nanoparticles by air indicated by the color change from red to blue. It was then investigated to use as a catalyst for Ullmann type amination coupling reactions of aryl chlorides [145]. A FCC Cu-Graphite (Cu@G) NP was synthesized using detonation decomposition method where Cu (OAc)2, H2, O2, CH2CH3OH were used as gas liquid mixtures. The TEM analysis conferred a spherical NP of core 10–40 nm with graphite layer shell of 4–8 nm. The resulting NP acted as a lubricant [146]. There are other Physical and Chemical Methods methods by which CuNPs can be synthesized. Some of them are given below in the table 3

Table 3: Physical and Chemical Methods for synthesis of Cupper Nanoparticles.

Type of Nanostructure synthesized	Chemical and Physical Methods	References
Nano Crystalline Cupper	Ball milling (assisted by Solid state reaction)	[147]
W–Cu nanocomposite	Tungsten carbide ball milling (Mechanical Milling)	[148]
Cupper Nanoparticle	Chemical reduction (Friedal Crafts Reaction)	[149]
Collidal Cupper Nanoparticle	Chemical Reduction (Polyallyl amine stabilized)	[150]
Nano crystalline Cu-Al alloy	Planetary ball mill	[151]
Crystalline Cupper nanoparticle	Chemical Vapor Nucleation	[152]
Nanocrystalline cupper	Sputtering and laser ablation	[153]
Cupper Nanoparticle	Flow-levitation method	[154]
Nanocrystalline Cupper	Solvated metal atom dispersion (SMAD) technique	[155]
Mixed-phase Ag–Cu nanostructures	Shadow nanosphere lithography with a glancing angle co-deposition technique	[156]
Cupper Nanoparticle	Ion Implantation	[157]
Cupper Nanoparticle	Matrix Sputtering Process	[158]
Cupper Nanoparticle	Continuous flow reactor	[159]
Cupper Nanoparticle	Vaccum vapour deposition	[160]
Cupper Nanoparticle	Waste Printed Circuit Board Recycling Method	[161]

3.0. Conclusion

There are various Physical and Chemical Methods used for the synthesis of cupper Nanoparticles. We have attempted to classify and cover a major portion of the non-biological methods that can be used for cupper nanoparticle synthesis including Pulsed laser ablation vacuum vapor deposition, pulsed wire discharge, mechanical milling, Microwave irradiation, Sonochemical approach, reverse micelles, microemulsion, Polyol method, Arc-Submerged Nanoparticle Synthesis System (SANSS), thermal decomposition, Chemical Reduction, Solvothermal Method, γ – irradiation, UV light irradiation, chemical reduction method and hydrothermal method. This review briefly explained the basic process involved in each method

4.0. References

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