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REVIEW PAPER

Synthesis of copper nanoparticles : An overview of the various methods

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Abstract−The synthesis of metal nanoparticles has received much attention due to their wide range of applications. Copper nanoparticles have attracted much attention due to their unique optical and electrical properties. Copper is relatively cheap in comparison to precious metals like gold and silver and also has high antibacterial properties. This review gives a brief overview of the available research works considering the synthesis of copper nanoparticles by chemical, physical, and biological methods.

Keywords: Copper Nanoparticle, Synthesis, Chemical, Physical, Biological

INTRODUCTION

Copper and its alloys are now widely used in many branches of modern engineering. Pure copper's extensive scope of applications is a result of its high electrical and thermal conductivity in addition to high resistance to corrosion [1].

In recent decades, metallic nanoparticles have been widely used in various industries due to their wide range of applications [2]. They have unique electrical, physical, chemical, and optical properties [3]. Copper nanoparticles have been considered by many researchers in the past two decades due to special features including optical/electrical properties [4].

For centuries, copper and its compounds have been used as disinfectants due to their antibacterial as well as antiviral properties [5]. The high surface-to-volume ratio of copper nanoparticles, like other metallic nanoparticles, yields in very high antibacterial properties [6]. Two groups of researchers [7,8], using single bacterial strains of Escherichia coli and Bacillus subtilis, proved that the antibacterial properties of copper nanoparticles are higher than those of silver nanoparticles. Moreover, non-agglomerated spherical, uniform copper nanoparticles are used in lubrication, as nano-fluids, catalysts, etc [9,10]. Thus, in view of the wide variety of applications of copper nanoparticles, synthesis is highly regarded. Generally, nanoparticles are synthesized through three different kinds of methods: chemical, physical, and biological [11]. Among all methods used to synthesize copper nanoparticles, we can refer to microemulsion, reverse micelles, gamma irradiation, ultraviolet irradiation, polyol process [12], sonochemical methods, thermal decomposition [13,14], laser irradiation [15], chemical reduction [16,17], microwave-assisted [18], and also biological methods in which living organisms such as plants [19], and bacteria [20] are used to synthesize copper nanoparticles. However, only some of the reported synthesis methods are capable of producing stable copper nanoparticles, due to the high oxidation rate of copper nanoparticles. Stable nanoparticles can only be produced in an inert atmosphere using nitrogen and argon gases to purge the reaction vessel. It has been reported that oxidation could occur upon exposure to air even after preserving the particle in an inert atmosphere [21]. Encapsulation of nanoparticles in organic or non-organic coatings like carbon and silicon can be used to prevent oxidation of copper nanoparticles [22,23]. Prucek et al. [24] produced stable copper nanoparticles that were resistant to oxidation by providing a non-polar media or previously deoxygenated polar media in an inert atmosphere [24]. Stable copper nanoparticles can also be synthesized in toluene, dodecanethiol, tridecylamine, with lauric acid as a protective agent and borohydride as reducing agent [25]. Another proposed method for the synthesis of stabilized copper nanoparticles is based on using high concentrations of a modifier such as polyethylene glycols, sodium dodecyl benzene sulfonate, sodium dodecyl sulfate or a mixture of two different types of modifiers and ascorbic acid as reducing agent [26]. Studies have also shown that the use of polyacrylic acid (PAA) as a stabilizer in the synthesis of copper nanoparticles by chemical reduction method leads to the production of stable copper nanoparticles.

SYNTHESIS OF COPPER NANOPARTICLES

1. Chemical Methods

Five different chemical synthetic procedures are reported so far for the synthesis of copper nanoparticles. Also, it is reported that growth and morphology of particles can be optimized by different factors such as temperature and concentration of the surfactant precursor [26].

1-1. Chemical Reduction Method

In the reduction method Cu (II) salts can be reduced by a variety of reducing agents, for instance: Hydrazine [27], Ascorbic acid [28], hypophosphite [29] or sodium borohydride [30] and polyol [31]. These reducing agents are used to produce copper nanoparticles with controlled size and morphology.

Gotoh et al. [32] reported using long-chain PAA (MW 150,000) to produce nanoparticles of Cu/PAA composite films that were deposited on glass plates [32]. Ostaeva et al. [33] managed to synthesize stable copper nanoparticles with a particle size less than 10 nm

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by reduction of Cu^{2+} in poly (acrylic acid)-pluronic blends solution [33]. Procek et al. [24] synthesized copper nanocrystals with a diameter of 14 nm using Cu reduction by sodium borohydride ions [24]. Chatterjee et al. [21] used $Cucl_2$ recovery in the presence of gelatin as stabilizers, without any special requirements (e.g., nitrogen purging) to synthesize stable copper nanoparticles with a size of 50-60 nm [21].

1-2. Microemulsion/Colloidal Method

Microemulsion is a technique to synthesize nanoparticles in which two immiscible liquids, (such as water-in-oil, oil-in-water or water-in-carbon dioxide supercritical) become a thermodynamically stable dispersion with the aid of a surfactant [16,34,35]. Reverse micelles method, which actually consists of two inverted emulsions of water and oil, is also placed in this category [36]. Salzemann et al. [37] used reverse micelles method to synthesize nanoparticles of copper with size of 3-13 nm [37]. Kaminskiene et al. [38] used the same technique to synthesize Cu colloidal solution with a size of 70-80 nm [38].

1-3. Photochemical Method

The microwave method is a form of electromagnetic energy in the frequency range between MHz300 to GHz300. Zhu et al. [39] found a rapid method for the synthesis of copper nanoparticles by using copper sulfate as a precursor and sodium hypophosphite as a reducing agent in ethylene glycol under microwave irradiation. The size of produced nanoparticles was reported to be 10 nm by the group [39]. Kapoor and Mukherjee [18] reached a mean size of 15 nm in synthesis of copper nanoparticles by using photochemical method with poly (N-vinylpyrrolido ne) as the stabilizer [18]. Giuffrida [40] used photochemical method for the synthesis of copper nanoparticles and found that the method is an appropriate way to synthesize copper nanoparticles, because it is convenient and economical. In this study, we found that different factors such as light intensity, sensitizer nature, concentration of surfactant polyvinyl pyrrolidone (PVP) could affect the size of nanoparticles. Light intensity is the key factor affecting the recovery rate of copper nanoparticles and is directly related to the reduction rate [40].

1-4. Electrochemical Method

In the electrochemical synthesis method for the production of copper nanoparticles, electricity is used as a controlling force. Electrochemical synthesis occurs by passing an electric current between two electrodes separated by an electrolyte. So synthesis takes place at the electrode/electrolyte interface. Usually, an electrolytic solution of copper salt and sulfuric acid is used for the production of copper nanoparticles [41]. Raja et al. [42] used copper sulfate and sulfuric acid as electrolytic solution and supplied 4 V, 5 A for 30 minutes and successfully synthesized Cu nanoparticles with the size of 40-60 nm [42].

1-5. Thermal Decomposition

In this method, the chemical reactions take place in a pressure and temperature controlled container like an autoclave, where the solvent reaches a temperature above its boiling point. If water is used as the solvent in this method then it is called a hydrothermal process [43,44]. Baco-Carles et al. [45] used this method for the synthesis of copper nanoparticles of 3.5-40 nm [45]. Chen et al. [46] applied hydrothermal method to synthesize copper nanoparticles with different sizes. They used surfactant sodium dodecyl benzenesulfonate (SDBS) to stabilize and control the shape and size of the nanoparticles. In this study we found that the reaction temperature and SDBS play important roles in shaping the final copper nanoparticles [46].

Table 1. Synthesis of copper nanoparticles by chemical methods

Method	Size nm	Ref.
Chemical reduction	2-10	[47]
Chemical reduction	5	[48]
Chemical reduction	100	[49]
Chemical reduction	3	[50]
Chemical reduction	45	[17]
Chemical reduction	70	[51]
Chemical reduction	3	[52]
Chemical reduction	50	[53]
Chemical reduction	DLS (20-100) HR-TEM, STEM, XRD (5-50)	[54]
Chemical reduction	>10 nm	[55]
Chemical reduction	30	[56]
Chemical reduction	2	[57]
Microemulsion/colloidal method	3-13	[37]
Microemulsion/colloidal method	70-80	[38]
Microwave method	10	[39]
Photochemical	15	[15]
Electrochemical	40-60	[42]
Electrochemical	8-12	[58]
Electrochemical	24	[59]

2. Physical Methods

2-1. Pulse Laser Ablation/Deposition

The laser ablation method is typically designed to produce colloidal silver nanoparticles in a variety of solvents. Nanoparticles are provided in colloidal form to prevent them from oxidation [60,61]. The pulse laser ablation process takes place in the chamber under vacuum and in the presence of some inert gases. In this method, the final product is influenced by some factors like the type of laser, the duration of pulsing and the type of solvent [42].

2-2. Mechanical/Ball Milling Method

The milling method makes some changes in the micron-sized material. Different types of milling machines are among the equipment used for the synthesis of nanoparticles in this method.

This method has some limitations, including difficulty in the production of ultrafine particles, which takes a long time. In contrast to these limitations, we can point to ease of operation, low production cost and enabling of large-scale production as the advantage of this method [62]. It has also been found that different factors determine the quality of the final product, i.e., the type of mill, milling speed, temperature, time, atmosphere, and container [63].

2-3. Pulsed Wire Discharge Method (PWD)

The pulsed wire discharge method is another physical method that can be used to synthesize nanoparticles [64,65]. This method is not typically used in industries due to its high cost and probable inefficiency for some metals. The method is appropriate for metals with high electrical conductivity, which can be easily formed into thin wires [41,66]. Muraia et al. [67] showed that copper nanoparticles coated with organic materials can be successfully synthesized

Table 2. Synthesis of copper nanoparticles by physical methods

Method	Particle size (nm)	Ref.
Pulse laser ablation/deposition	2-20	[73]
Pulse laser ablation/deposition	5-15	[74]
Pulse laser ablation/deposition	10-50	[75]
Pulse laser ablation/deposition	3-9 (small particles) 10-30 (larger particles)	[76]
Pulse laser ablation/deposition	5-30	[77]
Pulsed wire discharge method	62.2	[78]
Pulsed wire discharge method	27-72	[79]
Inert gas condensation	12	[80]
Exploding wire method	55	[81]

by evaporation of copper wire in oleic acid vapor/mist, and a coating layer with a few nanometers thickness. Using this method, the nano-sized particles were synthesized with the size of 10-25 nm [67]. Dash et al. [68] used (PWD) method by applying 22 KV power with 3 μF capacitance under the pressure of 0.1 MPa and synthesized Cu nanoparticles with the size of 16.11-43.06 nm [68]. Among the physical methods we can also refer to mechanochemical synthesis [69-71] and metal-organic chemical vapor condensation [72].

The general disadvantages of physical methods are that they usually require costly vacuum systems or equipment to prepare nanoparticles [41].

3. Biological Methods

It has been found that living organisms such as bacteria, fungi, and plants have a great potential for the synthesis of metal nanoparticles. Microorganisms act as a biofactory and can also be used for the synthesis of metal nanoparticles. In addition, researchers prefer biological synthesis, because in this method it is easier to control the size of synthesized nanoparticles distribution compared to other methods [82,83]. Unlike chemical methods, there is no toxic impact on the environment [82,83]. Understanding the mechanisms involved in the biosynthesis of metal nanoparticles is so important in order to have a better control over the process of producing metal nanoparticles [84].

3-1. Using Bacteria

Ramanathan et al. [85] used a biological method to synthesize copper nanoparticles using Morganella bacteria and under aqueous physiological conditions [85]. Varshney et al. [86] used a rapid biological method with a non-pathogenic bacterium of Pseudomonas stutzeri to synthesize copper nanoparticles. Studying the nanoparticles produced by the method using high resolution transmission electron microscopy (HRTEM) showed that nanoparticles are spherical in a size range of 8-15 nm [86]. Varshney et al. [87] also used Pseudomonas stutzeri to synthesize copper nanoparticles from wastewater generated from electroplating. They have a cubic shape and the size of nanoparticles produced by this method is 50-150 nm [87].

3-2. Using Fungi

Previous studies have found that NADH and NADPH dependent enzymes are important factors in the biosynthesis of metal nanoparticles [82]. Among the advantages of using fungal species for the synthesis of metallic nanoparticles are being economical, ease of the synthesis process and also the possibility of coating large surfaces due to the growth of fungal species. Pavani et al. [88] used Aspergillus species of fungus for the synthesis of Cu nanoparticles [88].

Table 3. Shows synthesis of copper nanoparticles by different organisms

Organism	Size (nm)	Ref.
Bacteria (Pseudomonas stutzeri)	8-15	[86]
Bacteria (Pseudomonas stutzeri from electroplating waste	50-150	[87]
Plant (magnolia leaf extract)	40-100	[94]
Plant (Syzygium aromaticum (Cloves) Aqueous Extract)	5-40	[96]

3-3. Using Plants

The use of various plants for metal nanoparticle synthesis has been studied by many researchers due to its low cost, high availability, and use of non-hazardous materials [89-91]. Positive results have been obtained. Bio-extracts often include metabolites such as flavonoids, proteins, terpenoids, polyphenols, etc. Not only do these biomolecules act just as reducing agents, but also they are used as capping agents to minimize particles accumulation, control morphology and also protect and stabilize produced nanoparticles [91]. Bali et al. [92] were able to synthesize different kinds of nanoparticles including copper nanoparticles in plants like Brassica juncea (Indian mustard), Medicago sative (Alfa alfa) and Helianthus annus (Sun flower) [92].

Lee et al. [19] used magnolia leaf extract as reducing agent and conversion of $Cu^{+2} \rightarrow Cu^{0}$ for synthesis of stable copper nanoparticles with a size of 40-100 nm. They used $CuSO_4 \cdot 5H_2O$ in aqueous solution and leaf extract to produce stable copper nanoparticles [19]. Valodkar et al. [94] used stem latex of Euphorbia nivulia, which is a plant with medicinal properties for synthesis of copper particles [94]. Subhankari and Nayak [95] used Ginger (Zinngiber officinale) to reduce copper sulfate and produce copper nanoparticles as a method for synthesis of copper nanoparticles, and they also analyzed the anti-bacterial effect of produced nanoparticles [95]. In a distinct article, Subhankari and Nayak in [96] used Syzygium aromaticum (cloves) in an aqueous extract for synthesis of spherical copper nanoparticles with 5-40 nm size. The study identified that existing biomolecules in bio-copper not only reduce metal ions, but also they prevent oxidation through stabilization of produced copper nanoparticles [96].

CONCLUSION

Three different methods for synthesis of copper nanoparticles were examined. Studies have shown that the size, morphology, stability, and properties are subject to experimental conditions. Chemical methods are the most frequently used methods for preparation of nanoparticles. The reducing agent used in synthesis is a key factor that can affect the size of nanoparticles and the reaction time. The time of the reduction process can vary from a few minutes to longer than 24 hours depending on the reaction conditions and the reagents used. The major disadvantage of the chemical methods is the toxic chemicals that are required in the synthesis and also the disposal of these reagents.

Physical methods are usually fast and do not involve toxic chemicals. The process of preparing nanoparticles using physical methods is faster than chemical and biological ones. The general disadvantage

of physical methods is the high cost of equipment to prepare the nanoparticles.

Preparation of nanoparticles takes typically much longer in the biological method compared to the physical and chemical methods. But, in some organisms the reaction time can reduce to a few minutes. The use of microorganism in the synthesis of nanoparticles is very eco-friendly. Given that biological methods are cheaper, more environmentally friendly, and easier to use, they offer a greater variety of potential methods of new routes of synthesis of copper nanoparticles.

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