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A REVIEW ON SYNTHESIS OF SILVER NANOPARTICLES

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Abstract:
Silver Nanoparticles (NPs) are of great interest in today's field of science due to their wide range of applications in various fields of industry. A variety of preparation techniques have been reported for the synthesis of silver Nanoparticles (NPs); examples include, laser ablation, gamma irradiation, electron irradiation, chemical reduction, photochemical methods, microwave processing, and biological synthetic methods. This review presents an overview of silver Nanoparticles preparation by physical, chemical, and biological synthesis. The aim of review article is, therefore, to reflect on the current state and future prospects, especially the potentials and limitations of the above-mentioned techniques for industries.

Key Words: *Nanoparticle synthesis, Silver Nanoparticles, Physical synthesis, Chemical synthesis, Biological synthesis.*

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INTRODUCTION:

Over the past few decades, Nanoparticles of noble metals such as silver and gold exhibited significantly distinct physical, chemical and biological properties from their bulk counterparts. Nano-size particles of less than 100 nm in diameter are currently attracting increasing attention for the wide range of new applications in various fields of industry [1]. Nanotechnology is an important field of modern research dealing with synthesis, strategy and manipulation of particle structures ranging from approximately 1-100 nm. Nanoparticles (NPs) have wide range of applications in areas such as health care, cosmetics, food and feed, environmental health, mechanics, optics, biomedical sciences, chemical industries, electronics, space industries, drug-gene delivery, energy science, optoelectronics, catalysis, single electron transistors, light emitters, nonlinear optical devices, and photo-electrochemical application. [2-6].

Nowadays, there is a growing need to develop eco-friendly processes, which do not use toxic chemicals in the synthesis protocols. Green synthesis approaches include mixed-valence polyoxometalates, polysaccharides, Tollens, biological, and irradiation method which have advantages over conventional methods involving chemical agents associated with environmental toxicity. Selection of solvent medium and selection of eco-friendly nontoxic reducing and stabilizing agents are the most important issues which must be considered in green synthesis of NPs.as outlined in figure1.

This review article presents an overview of silver Nanoparticle preparation by physical, chemical, and green synthesis approaches.

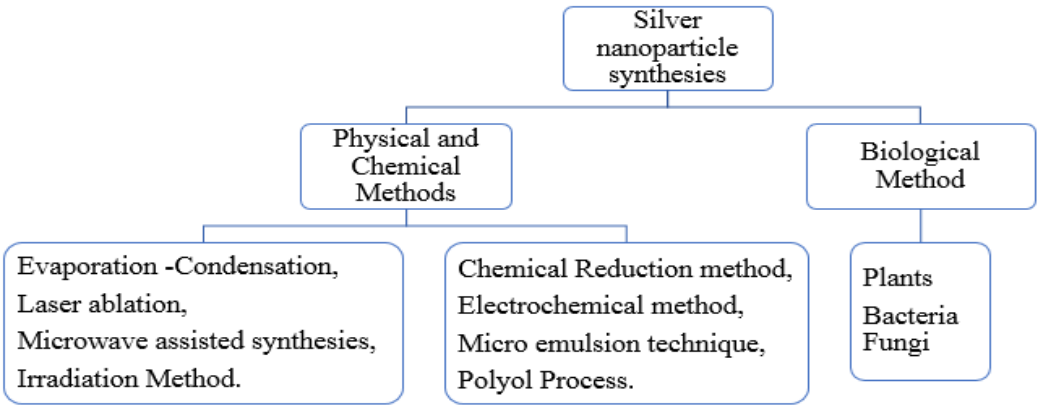

Fig .1: Flowchart on methods for synthesis of silver Nanoparticles

PHYSICAL METHODS:

Evaporation-condensation and laser ablation are the most important physical approaches. The absence of contamination in the prepared thin films and the uniformity of the NPs distribution are the advantages of the physical synthesis methods in comparison with the chemical processes. Physical synthesis of silver NPs using a tube furnace at atmospheric pressure has some disadvantages.

Evaporation-condensation Method: It was demonstrated that it could be synthesized via a small ceramic heater with a local heating area. The small ceramic heater was used to evaporate source materials. The evaporated vapor can be used at a rapid rate, because the temperature is in the vicinity of the heater.

In high concentration, this makes the formation of small NPs possible. The particle generation is very stable, because the temperature of the heater does not fluctuate with time. This physical method can be used as a nanoparticle generator for long-term experiments for inhalation toxicity studies, and the geometric standard deviation and the total number NPs increase with heater surface temperature. Spherical NPs without agglomeration were observed. The geometric mean diameter and the standard deviation of silver were in the range of 6.2-21.5 nm and 1.23-1.88 nm, respectively.

Laser ablation Method: NPs could be synthesized by laser ablation of metallic bulk materials in solution[7]. The ablation efficiency and the product of Nano-silver particles depend upon many parameters, including the wavelength of the laser impinging the metallic target, the duration of the laser pulses (in the femto-, pico- and nanosecond regimen), the laser fluence, the ablation time and the effective

liquid medium, with or without the presence of surfactants [8].

One important advantage of ablation technique.[9]. Silver nanospheroids (20-50 nm) were prepared by laser ablation in water with femtosecond laser pulses at 800 nm. The formation efficiency and the size of colloidal particles were compared with those of the colloidal particles prepared by nanosecond laser pulses. As a result, the formation efficiency for femtosecond pulses was significantly lower than that for nanosecond pulses. The size of colloids prepared by the femtosecond pulses were less dispersed than that of the colloids prepared by nanosecond pulses. Furthermore, it was found to be in the case of nanosecond pulses, the ablation efficiency for femtosecond was in the water and air.

Microwave-assisted synthesis: A method with good prognosis for the creation of SNPs is microwave-assisted synthesis. With the formation of NPs formed with NPs, formed of reduced volume, higher degree of crystallization and smaller sizes as compared to conventional oil baths. shorter time of production [10]. This technique with help from non-hazardous media decreases the chemical waste and time of reaction in many chemical alterations and many organic syntheses29. Carboxymethylselilo sodium can be used as a stabilizing and reducing agent for the synthesis of SNPs by this process route. SNPs were stable and uniform at room temperature for 2 months [11]. It was also reported to be the creation of ethylene glycol and polyvinyl pyrrolidine in the presence of platinum seeds [12].

Irradiation method: Silver NPs can be synthesized by using a variety of irradiation methods. Laser irradiation of an aqueous solution of silver salt and surfactant can produce NPs with a well-defined shape and size distribution [13]. Furthermore, laser was used in photosensitization of synthetic method of making silver NPs using benzophenone. At low irradiation times, low laser powers produced silver NPs of about 20 nm, while an increased irradiation power produced NPs of about 5 nm. Laser and mercury lamp can be used as light sources for production of silver NPs [14]. In visible light irradiation studies, photosensitized growth of silver NPs using thiophene (sensitizing dye) and silver nanoparticle formation by illumination of Ag (NH3) + in ethanol has been done [15,16].

CHEMICAL METHODS:

Chemical reduction: The most common approach for synthesis of silver NPs is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride (NaBH4), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol) -block copolymers are used for reduction of silver ions (Ag +) in aqueous or non-aqueous solutions. These reducing agents reduce Ag +, which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloid silver particles[17,18]. It is important to use protective agents to stabilize dispersive NPs during the course of metal nanoparticle preparation, and protect the NPs that can be absorbed on or bind onto nanoparticle surfaces, avoiding their agglomeration[19]. The presence of surfactants comprising functionalities (e.g. Thiols, amines, acids, and alcohols) for interactions with particle surfaces, and protect particles from sedimentation, agglomeration, or losing their surface properties.

Polymeric compounds such as poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and polymethylmethacrylate have been reported to be effective protective agents to stabilize NPs. In one study, Oliveira and co-workers[20] prepared dodecanethiol-capped silver NPs, according to Brust procedure 40 based on a phase-by-step transfer of an AU3 + complex from aqueous to organic phase into a two-phase liquid-liquid system, which was followed by a reduction with sodium borohydride in the presence of dodecanethiol as stabilizing agent, binding on the NPs surfaces, avoiding their aggregation and making them soluble in certain solvents. They are reported as "small changes in synthetic factors" to "nanoparticle structure", "average size", "size distribution width", "stability and self-assembly patterns". Kim and colleagues[21] reported synthesis of spherical silver NPs with a controllable size and high monodispersity using the polyol process and a modified precursor injection technique. In the precursor injection method, the injection rate and reaction temperature were important factors for producing uniform-sized silver.

Silver NPs with a size of 17 ± 2 nm were obtained at an injection rate of 2.5 ml / s and a reaction temperature of 100 ° C. The injection of the precursor solution into a hot solution is an effective means to induce rapid nucleation in a short period of time, ensuring the fabrication of silver Zhang and co-workers[22] used to hyper branched poly (methylene bisacrylamide aminoethyl piperazine) with terminal dimethylamine groups (HPAMAM-N (CH3) 2) to produce colloids of silver. The amide moieties, piperazine rings, tertiary amine groups and the hyper-

branched structure in HPAMAMN (CH3) 2 are important to its effective stabilizing and reducing abilities. Chen and colleagues43 have shown the formation of monodispersed silver NPs using the simple oleylamine-liquid paraffin system. Growth formation, incubation and Oatwald ripening stages. The higher boiling point of 300 ° C of paraffin affords a broader range of reaction. Moreover, the size of the colloid silver can not be regulated by the heating temperature, or the ripening time, but also by adjusting the ratio of oleylamine to the silver precursor.

Silver NPs can be prepared at room temperature, by simple mixing of the corresponding metal ions with reduced polyoxometalates which serves as reducing and stabilizing agents. Polyoxometalates are soluble in water and have the capability of undergoing stepwise, multielectron redox reactions without disturbing their structure. It was demonstrated that silver was produced by illuminating a deaerated solution of polyoxometalate / S / Ag + [23]. Further, green chemistry-type one-step synthesis and stabilization of silver nanostructures with mixed-valence polyoxometalates in water at room temperature has been reported[24].

Micro emulsion technique: Uniform and size controllable silver NPs can be synthesized using microemulsion techniques. The NPs preparation in two-phase systems is based on the initial spatial separation of reactants (metal precursor and reducing agent) in two immiscible phases. Inter-phase transport between two phases, which is mediated by a quaternary alkyl-ammonium salt, affects the rate of interactions between metal precursors and reducing agents. Metal clusters formed into the non-polar aqueous medium, and transferred to the organic medium by the inter-phase transporter[25]. One of the major disadvantages is the use of highly deleterious organic solvents.

Thus, large amounts of surfactant and organic solvent must be separated and removed from the final product. For instance, Zhang and co-workers[26] used Dodecanese as oily phase, but there was no need to separate the prepared silver solution from the reaction mixture. On the other hand, colloid NPs prepared in a nonaqueous medium for conductive inks are well dispersed in a low vapour pressure organic solvent, to be readily wet the surface of polymeric substrate without any aggregation. NPs as catalysts to catalyze most organic reactions, which have been conducted in non-polar solvents. NPs to different physicochemical environments in practical applications.

Electrochemical method: An electrochemical procedure, based on the dissolution of a metallic anode in an aprotic solvent, has been used to obtain silver Nanoparticles ranging from 2 to 7 nm. It is possible to obtain different silver particle sizes. Silver polarization in a non-aqueous solution of NaNO3in ethanol was investigated by means of cyclic voltammetry and chronoamperometry. A deposit consisting of metallic silver Nanoparticles has been obtained by both potentiostatic and galvanostatic method. The proposed mechanism assumes both anodic dissolution of silver and its reduction to the metallic state during polarization in ethanol. Producing process is a new and very simple method of producing silver Nanoparticles.

Polyol process: Spherical silver Nanoparticles with various sizes and standard deviations were synthesized by the polyol process. It involves the use of two methods. The precursor injection method, in which a silver nitrate aqueous solution will be injected into hot ethylene glycol. Because of rapid nucleation and injection rate silver Nanoparticles with a size of 17 ± 2 nm were obtained at an injection rate of 2.5 ml s-1. Continuous-flow single-mode microwave reactor was used in polyol process. The synthesis is exceptionally effective. Silver acetate is able to synthesise small spherical Nanoparticles in few seconds[27].

Disadvantages of using physical and chemical methods: The synthesis of Nanoparticles via physical and chemical processes is very much cost effective. This method requires strong and weak chemical reducing agents as well as capping agents like sodium borohydride, sodium citrate and alcohols. These agents are generally highly toxic, flammable; cannot be easily disposed. Hence green syntheses of Nanoparticles are now commonly preferred to use microorganisms and plant extracts as they are relatively economical, nontoxic and eco-friendly.

Biological methods: The synthesis of Nanoparticles by chemical approaches are eco-unfriendly and expensive. Thus, there is a growing need to develop environmentally and economically friendly processes, which do not use toxic chemicals in the synthesis protocols. This has led researchers to look at the organisms. The potential of organisms in Nanoparticle synthesis ranges from simple prokaryotic bacterial cells to eukaryotic fungi and plants[28].

Biological methods could be used for synthesis of highly stable and well characterized NPs when critical aspects, such as types of organisms, inheritance and genetic conditions of organisms, optimal conditions

for cell growth and enzyme activity, optimal reaction conditions, and selection of the biocatalyst state have been considered. Sizes and morphologies of the NPs can be controlled by altering some critical conditions, including substrate concentration, pH, light, temperature, buffer strength, electron donor (e.g., glucose or fructose), biomass and substrate concentration, mixing speed, and exposure time.

Plants: This green chemistry approach toward the synthesis of silver Nanoparticles has many advantages such as, ease with which the process can be scaled up, economic viability, etc. Applications of such eco-friendly Nanoparticles in bactericidal, wound healing and other medical and electronic applications, makes this method potentially exciting for the large-scale synthesis of other inorganic materials (nonmaterial's). In the following section,(Table1) we discussed the synthesis of silver Nanoparticles by using various plants and their parts as shown in (fig.3).

Table 1: Synthesis of silver Nanoparticles from different medicinal plants.

Plants	Size in nm	Plant Part	References
Cremona Mexicana	30	Leaves	A Singh et al[29].
Azadirachta indica	20	Leaves	Shankar et al.[30]
Alpine galangal	20.82	Rhizome	Binna Mathew et al.[31]
Artocarpus heterophyllus	10.78	Seeds	Mesh B Jag tap. et al.[32]
Allemande cathartic	19-40	Leaves	M.lingaraoet al.[33]
Aloe Vera	70	Leaves	Chandra et al.[34]
Carica papaya	20-25	Fruit	Jain et al.[35]
Capsicum annum	25-50	Leaves	Shikuo Li et al.[36]
Cinnamon zeylanicum	30-50	Bark	M Sathishkumar etal.[37]
Coffee Arabica	20-50	Leaves	Mallikarjuna et al.[38]
Citrus sinensis	10-35	peel	Kaviya et al.[39]
Citruscolocynthus(bitter apple)	75	Callus	K Satyavani et al.[40]
Catharanthus roseus	35-55	Leaves	Gondwal et al.[41]
Datura metel	16-40	Leaves	Kesharwani et al.[42]
Eucalyptus hybrid	50-100	Leaves	Manish Dubey etal.[43]
Jatropha curcas	10-20	Latex	Harekrishna Bar et al.[44]
Malus domestica	20	Fruit	K.roy et al.[45]
Murraya koenigii	10-25	Leaves	Laura Christensen etal.[46]
Mangrove plant	60-95	Leaves	M. Gnanadesigan et al.[47]
Ocimum sanctum	44-30	Leaves	Garima Singhal et al.[48]
Pinus eldarica	10-40	Bark	Santhoshkumar et al.[49]
Premna serratifolia	22.97	Leaves	J. Arockia John Paul et al.[50]
Premna herbacea	10-30	Leaves	Kumar et al.[51]
Psoralea corylifolia	100-110	Seeds	Sunita et al.[52]
Thevetia peruviana	10-30	Latex	Rupiasih et al.[53]
Trianthema decandra	15	Root	R. Geethalakshmi et al.[54]
Tinospora cordifolia	10-25	Leaves	J. Chidambaram et al.[55]
Vitex negundo	5 and 10-30	Leaves	Ericka Rodriguez-Leon et al.[56]

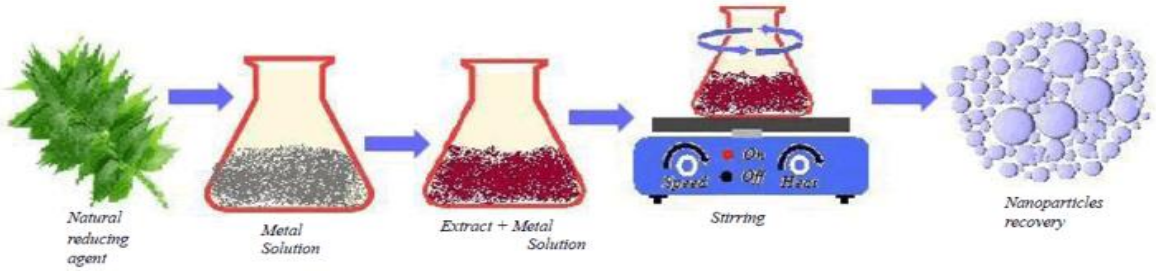

Fig.2: Preparation of silver Nanoparticles from plants

Catharanthus roseus [41] is used for the synthesis of silver Nanoparticles having antiplasmodial activity against Plasmodium falciparum. A recognition–reduction–limited nucleation and growth model was used to explain the possible formation mechanism of silver NPs which were synthesised using Capsicum annuum L. extract[36]. Synthesis of silver Nanoparticles using Coffee Arabica [38] was done using a single pot method which does not require any surfactant and a capping agent. Synthesis of silver Nanoparticles can be done by reducing the silver ions present in the solution of silver nitrate by the cell free aqueous extract of Carica papaya [35].

The Cinnamonum zeylanicum [37]bark extract and powder are a good bioresource/ biomaterial for the synthesis of Ag Nanoparticles with antimicrobial activity. The flavonoid and terpenoid constituents which were present in Eucalyptus hybrid [43]leaf extract can be used as surface active molecules stabilizing the Nanoparticles. Such rapid scale synthesis of silver NP's proves that natural sources can be used as prominent alternatives for altering the chemical processes. Silver Nanoparticles were successfully synthesized from AgNO3 using the latex of Jatropha curcas[44]as reducing as well as capping agent. This method involves production of bulk quantities of Nanoparticles using noble metals like Ag and Pd. Trianthema decandra[54] root extract is used for synthesis of Nanoparticles of 15nm size. Cost effective and environment friendly technique for green synthesis of silver Nanoparticles from 5mM AgNO3 solution through the extract of Argemone maxicana [29]leaf extract as reducing agent as well as capping agent. Nanoparticles were characterized using UV–Vis absorption spectroscopy, FTIR, XRD and SEM. X-ray diffraction and SEM analysis showed the average particle size of 30 nm as well as revealed their structure.

These Nanoparticles act as both reducing and stabilizing agents in various antibacterial products. Using Ocimum sanctum[48] Nanoparticles of about 4 to 30 nm can be synthesized in an ecofriendly manner. Nanoparticles synthesized using Tinospora cordifolia[55] showed activity against lice. The reduction of the metal ions through the callus extracts of Citrus colocynthus[40] leading to the formation of the silver Nanoparticles of fairly well - defined dimensions. The green chemistry approach towards the synthesis of silver Nanoparticles have many advantages. Applications of such eco-friendly Nanoparticles in bactericidal, wound healing and other medical fields and electronic fields. Nano-silver particles with an average size of 18.2 ± 8.9 nm and spherical shapes were synthesized using methanolic extract of Vitex negundo[56] leaf.

The size of silver Nanoparticles synthesized using *Alpine galangal[31]* rhizome extract was about 20nm and particles formed using this extract anti-microbial and catalytic activity. *Azadirachta indica[30]* aqueous leaf extract was used to synthesise Nanoparticles with antibacterial activity against Gram + ve and Gram-ve organisms. These have shown peak absorbance at 436-446 nm.

Bacteria: Inorganic Nanoparticles like silver, gold, silicon oxide, magnesium, cadmium sulphide can be synthesized by many organisms. The resistance for silver ions caused by the bacterial cell in their environment is responsible for Nanoparticles synthesis [57].

The primary proof of microorganism synthesizing silver Nanoparticles was established by the bacterium bacteria genus Pseudomonas stutzeri AG259 strain that was isolated from mine[58].The important and widely accepted mechanism of silver biogenesis is that the presence of the enzyme nitrate reductase [59]. The accelerator converts nitrate into nitrite. In vitro synthesis of silver by microorganisms, the presence of alpha nicotinamide purine dinucleotide phosphate reduced kind (NADPH) -dependent nitrate protein would remove the downstream method step that is required in different cases[60].

Throughout the reduction, nitrate is regenerated into cluster and conjointly the lepton is transferred to the silver ion; hence, the silver particle is reduced to silver (Ag + to Ag0). Various bacteria (Table.2) is used for the synthesis of silver Nanoparticles Pseudomonas stutzeri [64], Bacillus megaterium[61], Enterobacter cloacae[62], Escherichia coli[63].

Table 2: Synthesis of silver Nanoparticles from different Bacteria.

Biological source	NP's produced	NP's size	References
Bacillus megaterium	Ag	5-60 nm	Saifuddin *et al.*[61]
Enterobacter cloacae	Au	15-30 nm	Husseiny *et al.*[62]
Escherichia coli	Pd	20-50 nm	Deplanche and Macaskieet al.[63]
Pseudomonas stutzeri	Ag	40 nm	Deplanche *et al.*[64]

fungi: If a comparison of fungi is made with bacteria then a larger amount of Nanoparticles is a result of secreting large amounts of proteins that directly translate to higher productivity of Nanoparticles.

The mechanism of silver nanoparticle production by fungi is purported to the subsequent steps: trapping of Ag + ions at the surface of the fungal cells and additionally the next reduction of the silver ions by the enzymes gift at intervals the fungal system. The accelerators like NADPH-dependent nitrate reductase and a shuttle quinine extracellular process are a unit responsible for nanoparticle formation[65]. A significant disadvantage of the microbes to synthesize silver Nanoparticles is that it is an extremely slow technique once compared with plant extracts.

Hence, the employment of plant extracts to synthesize silver Nanoparticles becomes associated with chance that is potential. Various fungi (Table.3) used for the synthesis of silver Nanoparticles are Verticillium sp.[68], Fusarium semitectum[67], Aspergillus fumigates[66],

Table 3: Synthesis of silver Nanoparticles from different Fungi

Biological source	NP's produced	NP's size	References
Aspergillus fumigates	Ag	5-25 nm	Ratnasri et al.[66]
Fusarium semitectum	Ag	20-25 nm	Basavaraja *et al.*[67]
Verticillum sp.	Ag	20.25 nm	Mukherjee *et al.*[68]

Applications of Nanoparticles: Novel applications of Nanoparticles and Nanomaterials are growing rapidly on various fronts due to their completely new or enhanced properties based on size, their distribution and morphology. It is swiftly gaining renovation in a large number of fields such as plasmatic and photovoltaic's, health care, cosmetics, biomedical, anti bacterial, food and feed, drug-gene delivery, environment, health, mechanics, optics, chemical industries, electronics, space industries, energy science, catalysis, light emitters, single electron transistors, nonlinear optical devices and photo-electrochemical applications[69].

- Treatment of ulcerative colitis & acne
- Treatment of dermatitis
- Inhibition of HIV-1 replication
- Enhanced Raman Scattering Spectroscopy (SERS)
- Detection of viral structures (SERS & silver nimrods)
- Antimicrobial effects against infectious organisms
- Remote laser light-induced opening of microcapsules
- Silver/dendrite nanocomposite for cell labelling
- Molecular imaging of cancer cells
- Coating of hospital textile (*e.g.*, surgical gowns & face mask)
- Coating of catheter for cerebrospinal fluid drainage
- Coating of surgical mesh for pelvic reconstruction
- Coating of breathing mask patent
- Coating of endotracheal tube for mechanical ventilatory support
- Coating of driveline for ventricular assist devices
- Coating of central venous catheter for monitoring
- Coating of intramedullary nail for long bone fractures
- Coating of implant for joint replacement
- Orthopaedic stockings/ Additive in bone cement
- Implantable material using clay-layers with starch-stabilized silver NPs
- Superabsorbent hydrogel for incontinence material/ Hydrogel for wound dressing
- Additive in polymerizable dental materials patent
- Silver-loaded SiO2 nanocomposite resin filler (Dental resin composite)
- Polyethylene tubes filled with fibrin sponge embedded with silver NPs dispersion

CONCLUSION:

In this review, different methods to prepare AgNPs and their properties as well as applications are presented. In particular, several novel chemical methods based on our recent studies are described, which are successful in the synthesis of AgNPs with high conductive properties. The reaction mechanism of AgNPs and factors affecting particle size are also clarified. Significant advantages of these methods over previous ones include: it has a short reaction time; relatively uniform particles with small diameter are produced; the reaction proceeds rapidly at room temperature; organic solvents are not used, and used chemical reagents are water soluble, cheap, easy to deal with, not producing hazardous by-products and environmentally friendly; and the resulting particles are easily separated from the reaction mixture. Therefore, these approaches can contribute to saving energy and reduce the cost of preparing AgNPs. These methods are also safe and environmentally benign, which are very important factors from the perspective

of industrial manufacturing. Particularly, these advantages of these methods are very important to use AgNPs for medical applications because of non-toxicity. Therefore, these advantages make the present methods practically useful and potentially applicable to large-scale industrial manufacture of stable colloids silver Nanoparticles, which are applicable in various fields, especially digital fabrication of electronic circuits and medicinal applications.

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