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Review Article
Synthesis Pathway and Powerful Antimicrobial Properties of Silver Nanoparticle: A Critical Review

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Abstract
One of the most useful applications of silver nanoparticles (Ag-np) is an antimicrobial agent that can have inhibitory effects against microbial pathogens. This paper reviews the detail of physical, chemical and green chemistry methods for synthesis of Ag-np and also its mechanism as antibacterial to inhibit many microbial pathogens. The main steps in preparation of Ag-np via chemical and green chemistry methods are the choice of the solvent medium, reducing agent and stabilizing or capping agent. The physical method needs physical or mechanical energy to achieve nano-size material. Green chemistry is the most promising method to be developed due to its simplicity and environmentally benign. As an antibacterial agent, effects of Ag-np toxicity are influenced by both of Ag-np and the silver ions which released during contact with water or tissue fluid. Both of those silver species can penetrate into the cytoplasm, DNA or ribosomes. The inactivation process of enzyme-membranes like phosphomannose isomerase caused denaturation of the bacterial cell.

Key words: Silver nanoparticles, inhibitory, antibacterial, reducing agent, stabilizing agent, green chemistry

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Nowadays, nanotechnology has interesting attention in modern research due to its useful application for human being and effort to control material size in nanometer scale. Nanomaterials are all materials which have 1-100 nm in size[1]. They have the unique properties compared to their macro scale due to their high surface area and plasmon excitation phenomenon[2,3].

In addition to semiconductor[4] and some new intermetallic compounds[5-7], the silver nano-particle (Ag-np) has attracted tremendous interest in last two decades. Ag-np has an advantage compared to other metal nano-particles for a photochemical application. For example, the extinction coefficient for plasmon absorption for a 20 nm Ag-np is $4.75\times10^{9}\,M^{-1}\,cm^{-1}$, whereas for Au-np is $1\times10^{9}\,M^{-1}\,cm^{-1}$ [8]. In the other word, Ag-np is more reactive than the other one to produce plasmon excitation process in nano-particles reaction with photon. Furthermore, Ag-np can also be combined with semiconductor materials or other materials for a particular purpose.

Ag-np is widely applied in human daily need, like in textile clothes[9], water filters and purifications systems[10], toothpaste[11], toys[12], etc. mainly due to their antibacterial properties[13]. As antibacterial agent, Ag-np has shown the activity to inhibit both of Gram-positive and Gram-negative bacteria, such as *S. aureus*[14], *E. coli*[15,16] and *K. pneumonia*[17]. The optical properties of Ag-np depend on its size. So, many efforts to synthesize Ag-np are very important.

In general, there are two ways to synthesize the nano-particles: the top-down and bottom-up methods. The top-down method refers to the synthesize route from the bulk materials by using physical and mechanical process. Whereas, the bottom-up method refers to the synthesize route from the small molecule precursors by using chemical reaction[18]. Until now, the bottom-up method dominates the synthesis procedure of nano-materials due to its simplicity.

The solid, liquid and gaseous phases can be used as precursor materials in the bottom-up method. However, precursors in the liquid phase are more widely used by researchers. The step to producing nano-particles with chemical reaction includes the selection of the solvent, the reducing agent and the stabilizing or capping agent. Specific control of shape and size distribution in the liquid phase is often achieved by varying the reducing agents and stabilizers[19,20].

The reducing agent (the reductant) is the compound that reduces the metal ions into the metallic forms. The active site of the reducing agent acts as an electron donor to produce the nano-particles[21]. The stabilizing agent refers to the compound that can be used to avoid the agglomeration of the nano-particles. There are two categories of stabilizing agents: the electrostatic and the steric stabilizers. The electrostatic stabilizers refer to many types of anionic species, such as halides or carboxylates that make coordination to metal nano-particles[22]. This phenomenon produces the electrical double layer with Coulomb repulsion between the nano-particles. On the other hand, the steric stabilizer is the bulky organic materials such as polymers or alkyl ammonium[23].

Nowadays, many researchers develop the new materials by using the biotemplate both as the reducing agent and stabilizing agent, which is called "Green chemistry" or biological methods. The biotemplate are more environmentally benign than inorganic precursor. The examples of the biotemplate are plant extracts[24], fungi enzymes[25], bacterial enzymes[26], algae extracts[27], etc.

In this study, the authors would like to overview the synthesis method of Ag-np, including physical, chemical and biological methods. Subsequent, the application of Ag-np in many terms of antimicrobial activity would be discussed detail.

SYNTHESIS PATHWAYS OF Ag-np

Physical method: Preparation of nano-particle materials can be carried out by physical methods, such as: High energy ball milling[28], electrical explosion wire[29], arc discharge[30], microwave[31], CO_2 laser radiation[32], spray drying[33], pulsed electron evaporation[34], laser ablation[35] and conventional evaporation-condensation[36]. The physical method needs less chemical reagent and does not produce the byproduct as impurities. Thus, the physical method is one of the best ways to prepare the pure colloid or nano-particle.

The laser ablation is frequently applied in the physical method for synthesis of Ag-np from bulk material[37-45]. The properties of the nano-particles produced by laser ablation route depend on some parameters, such as the wavelength of laser imprinting metal target, the laser fluency, the duration of laser pulses and the effective medium like surfactants or others[46,47].

Figure 1 shows the experimental apparatus of the laser ablation method[48]. Tsuji *et al.*[48] used Nd: YAG laser pulses as an energy source at 1064, 532 and 355 nm. They found that the nano-particles size could be controlled by changing laser ablation wavelength. The average diameter of synthesized Ag-np was 29, 26 and 12 nm for the wavelength source at 1064, 532 and 355 nm, respectively. The particles size was decreased when the laser wavelength also decreased. This

phenomenon was generated by the fragmentation of colloidal particles by self-absorption laser pulses.

Besides the laser ablation, another modern physical method to produce Ag-np is arc discharge. In general, the arc discharge is defined as a system which uses energy to convert the material in plasma form in the presence of high purity electrode system (usually titania). There are two types of arc discharge: gas arch discharge and liquid arc discharge. The gas arc discharge uses the inert gas as a reaction barrier, while the liquid arc discharge uses the liquid condition which immerses the electrode[49].

Conventional evaporation-condensation reaction at atmospheric pressure could also be performed for preparing nano-particle material. The source material is placed in the tube furnace and it is vaporized by using carrier gas[50,51]. The conventional evaporation-condensation method has several drawbacks. This process needs higher energy than other methods to raise the reaction temperature and also it needs longer reaction time to reach the thermal stability[52].

The most prospective physical method for synthesis Ag-np was high energy ball milling. The mechanical milling initiates deformation of the bulk crystal[28]. The high energy ball milling introduces the elastic strain energy into the initially bulk crystal through shearing actions of ball-powder collisions. The phenomenon produced the crystal defect (atomic vacancies and dislocations) and also atomic scale chemical disorder.

For example, Khayati and Janghorban[53] had reported the synthesis of Ag nano-powder by using high energy planetary ball milling. The precursors were Ag_2O powder as the source of Ag-np and graphite as an additional reducing agent. The rotation speed of disc and vial was 250 and 450 rpm, respectively. The weight ratio of the ball to powder was 20:1. The complete reaction occurred after 22 h indicated the absence of Ag_2O peak in the sample. The obtained silver nano-powder had the crystallite size of 28 nm and internal strain of 0.44%. The reaction in the process could be written as follow:

$$2\ Ag_2O + x\ C \rightarrow 4\ Ag + CO_2 + (x-1)\ C,\ x = 1.4$$

The physical method for Ag-np synthesis needs physical or mechanical energy. It commonly used for preparing Ag-np powder in the narrow size. However, the physical method is a high-cost process due to the use of modern instrument and requires high energy[54]. The comparison of different physical method to synthesize silver nano-particle are given in Table 1.

Chemical reduction method: Chemical reduction method is a general method which applied to obtain Ag-np. The chemical reduction reactions are carried out in solution and the product has colloidal characteristics. The common phenomenon which occurs in the chemical reduction reactions is co-precipitation. The step of this reactions involves reduction, nucleation, particle growth and/or agglomeration of the particle[55].

The most important aspect of chemical reduction method is the value of the standard reduction potential (E^0). It means

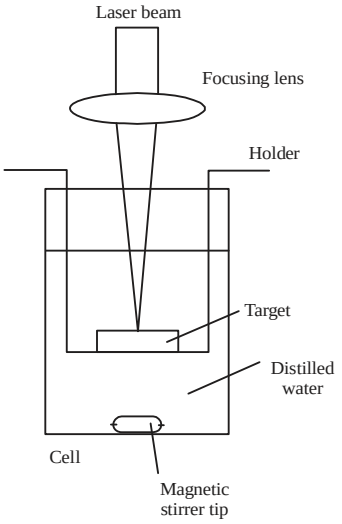

Fig. 1: Experimental set-up for colloidal preparation by laser ablation in solution based on Tsuji *et al.*[48]

Table 1: Comparison of different physical method to synthesize Ag-np

Methods	Advantages	Disadvantages
Conventional evaporation-condensation	Cheap instrumentation	Need the highest energy compared from other physical methods
		Take a long time to reach the thermal stability
Laser ablation	No need further sample preparation	Limited production yield or maximum area of the substrate that
	Small sample consumed	can be treated
	Non-destructive technique	Obtain irregular shape and size
	Low impurities	
Arc discharge	Can produce many nanotubes	Need other metal as an electrode
	High-throughput	Need inert gas as a gas carrier
Ball milling	Can be used in dry or wet condition	Running vibration and noise
	Low-cost investment	Large energy consumption
	Suitable for batch or continuous system	High electricity consumption
	Potential to develop in industrial scale	

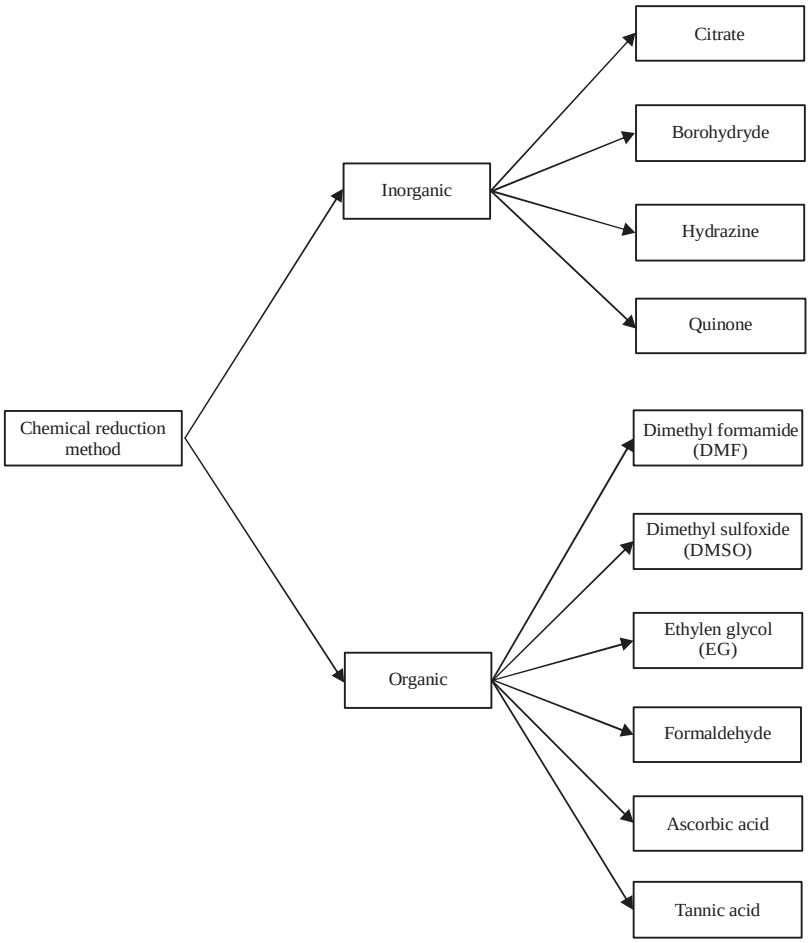

Fig. 2: Classification of some chemical reducing agents to synthesize the Ag-np

that the free energy (ΔG^0) change must be negative or equivalent to $\Delta E^0>0$. In the case of silver, the relatively large electropositive reduction potential of $Ag^+ \rightarrow Ag^0$ in water is +0.799 V[56]. Thus, there are some reducing agents that compatible with this condition to reduce silver ion into silver metal form. The common reducing agent are sodium citrate (E^0 = -0.180 V)[57], sodium borohydride (E^0 = -0.481 V)[56], hydroquinone (E^0 = -0.699 V)[58], etc.

In general, the reducing agent can be divided into two groups: the inorganic and organic reductants. Sodium citrate, sodium borohydride, hydrazine and hydroquinone are the examples of inorganic reductants[56-58]. While the examples of organic reductants are dimethylformamide (DMF)[59], dimethyl sulfoxide (DMSO)[60], ethylene glycol (EG)[61], formaldehyde[62], ascorbic acid[63], tannic acid[64], aniline[65], etc. The selection of the reduction agent influences the size of Ag-np. The strong reductant like sodium borohydride produces small particle[66]. Whereas the utilizing of some weak reductant such as sodium citrate makes slow reduction rate and produces larger particle[67]. The classification of some chemical reductants was expressed in Fig. 2.

Typically, the utilizing of the reductant is combined with the stabilizer agent to avoid nano-particle agglomeration. The stabilizer binds to the surface of the nano-particle, so it has no reaction between surfaces of each nano-particle. Small alterations in the synthetic parameters can influence the nano-particle's size, stability and shape[68].

Chemical reduction by using inorganic reductants: Turkevich invented utilization of citrate anion as a reduction agent[69] gold nano-particle was synthesized from $AuCl_4^-$ in aqueous solution at boiling temperature by using sodium citrate. After that research, many researchers became more interested in studying the mechanism and nano-particle growth by using citrate anion as a reductant.

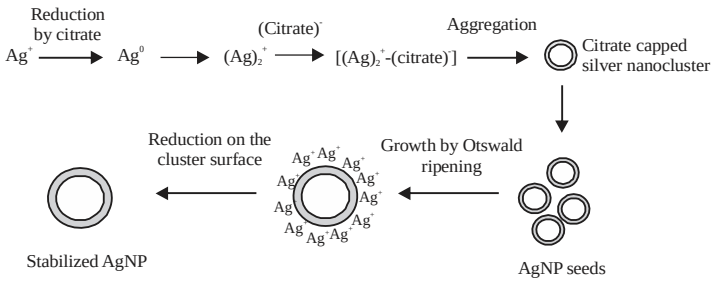

Fig. 3: Mechanism of Ag-np growth using citrate as reductant[67]

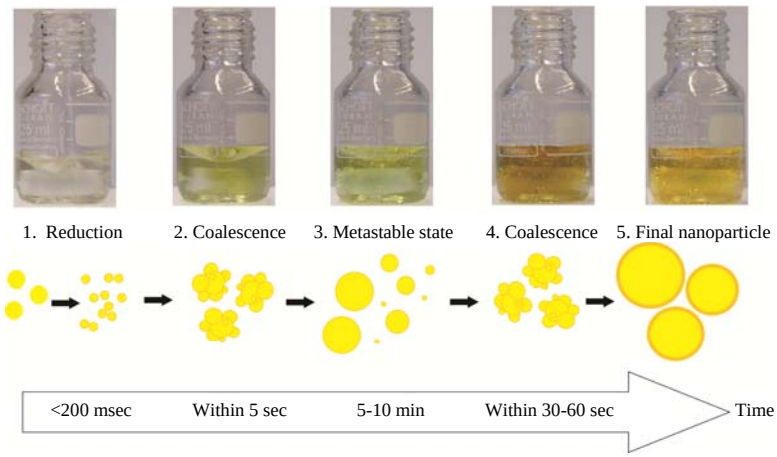

Fig. 4: Proposed mechanism of Ag-np growth using $NaBH_4$[71]

From prior research, it has been known that the citrate acted both to reduce the metal cation and to stabilize the formed nano-particles. It was also believed that the citrate played an important role in determining the growth of the nano-particles. The citrate anion triggered the slow crystal growth compared to other chemical and physical method. The large size of Ag-np resulted by slow rate reaction in citrate reduction method is approximately in range 50-100 nm. The mechanism can be illustrated in Fig. 3[67].

Furthermore, Suriati *et al.*[70] proposed formation of Ag-np using trisodium citrate as the reducing agent and ascorbic acid as a stabilizer. The first step in this mechanism was the reductant ($C_6H_5O_7Na_3$) directly reduced silver ions into silver atoms. The reduced silver atoms then acted as nucleation center and made the other silver ions reduced, so the nano-particles could growth through this nucleation center. When the color was changed from light yellow → yellow → greenish, it indicated the formation of stable Ag-np. The overall reaction of this process can be expressed as follow:

$$4Ag^{+}+C_6H_5O_7Na_3+2H_2O \rightarrow 4Ag^{0}+C_6H_5O_7H_3+3Na^{+}+H^{+}+O_2$$

As described before, the sodium borohydride ($NaBH_4$) was a stronger reductant than the citrate anion. The mechanism of Ag-np formation by using $NaBH_4$ was described below[71]:

$$M^{n+}+nBH^{-} \rightarrow M^{0}+n\ B(OH)_3+n\ 3.5\ H_2$$

The first mechanism was the reduction of Ag^{+} to Ag^{0} atoms. Because of $NaBH_4$ was a strong reductant, it needed a short time (<200 ms) to convert Ag^{+} to Ag^{0} atoms. These atoms formed dimers, trimers, clusters, etc. The second mechanism, the cluster coalesced to form small particles with average size 2-3 nm. This step is followed by metastable state and after 5-10 min it became stable size. The second coalescence has occurred within 30-60 s after the formation of stable particle size. The final product of this mechanism was Ag-np with average size 5-8 nm (Fig. 4)[71].

Chemical reduction by using organic reductants: The advantages of using the organic solvent in Ag-np synthesis are it can produce higher yield and smaller particle size of Ag-np. Rodriguez-Gattorno *et al.*[60] investigated Ag-np preparation by

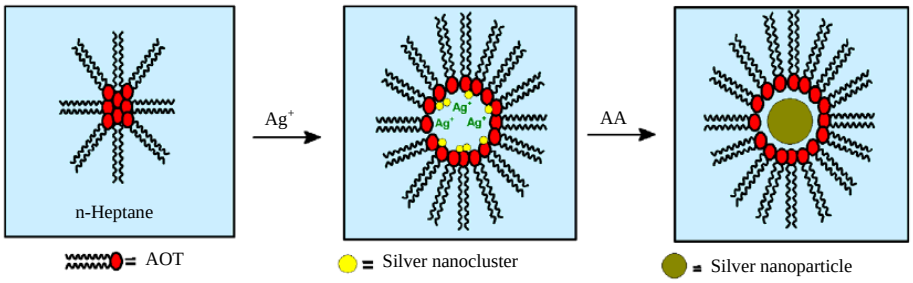

Fig. 5: A scheme representing the formation of Ag-np reverse micellar route proposed by Singha *et al.*[63]

using 2-ethylhexanoate [Ag(ethex)] as precursor and dimethyl sulfoxide (DMSO) as a reductant at room temperature. As a result, they could prepare very stable Ag-np with diameter size of 4.4 nm (SD = 1.2). The surface plasmon resonance of formed Ag-np was measured at 424 nm. The HR-TEM image showed that there was a high concentration of Ag-np morphology defects such as stacking faults and the multiple twinning. Based on the experimental data, the mechanism of Ag-np can be described as follows:

$$[AgOOCR]+DMSO \rightleftharpoons [AgOOCR\bullet DMSO]$$

$$[AgOOCR\bullet DMSO] \rightarrow Ag^0+[DMSO^{\bullet}]^+ +[:OOCR]^-$$

$$[AgOOCR]+[DMSO^{\bullet}]^+ \rightarrow Ag^0+[:OOCR]^- +[DMSO^{\bullet}]^{2+}$$

$$[DMSO^{\bullet}]^{2+}+2\ H_2O \rightarrow DMSO_2+2\ H^+$$

The overall reaction is written as follows:

$$2\ [AgOOCR]+DMSO+H_2O \rightarrow Ag^0+DMSO+[:OOCR]^-$$

While, R is $(C_2H_5)CH(CH_2)_3CH_3$.

The Ag-np was successfully prepared by using ascorbic acid ($C_6H_8O_6$) in dioctysulfoccinate (AOT) reverse micelles at room temperature[63]. The suggested reaction during this reduction process was follow:

$$C_6H_8O_6+2\ Ag^+ \rightarrow 2\ Ag+C_6H_8O_6+2\ H^+$$

Increasing the ascorbic acid concentration led the darken color solution as increasing the optical density of the plasmon resonance. The first mechanism of silver ions reduction by using ascorbic acid in reverse micelle was the formation of the silver nanocluster (Ag-nc). The silver ions were bound to the negative sulfonate group and form the Ag-nc in the micelle. Subsequent, in the presence of ascorbic acid as an electron donor, would trigger Ag-np growth (Fig. 5). The reverse micelle acted not only as a template but also accelerated the chemical reduction process due to the Ag-nc formation in the micelle[63].

The chemical reduction method is a simple and low-cost method for preparing Ag-np. This method can produce Ag-np in various shape and size. However, some precursors in the chemical reduction method are less favored due to the use of various inorganic compounds. Some of the inorganic precursors have harmful effect on the environment. Therefore, it is necessary to develop another method that uses pure organic or biological precursors.

Green chemistry method: Recent years, the researchers are developing the green chemistry method due to the elimination of hazardous materials compared to the conventional chemical reduction method[72]. This method is very popular because of its abundant material, simplicity, safety handle, low cost and also minimize the laboratory pollutant[73]. As a conventional methods, the main steps in the green chemistry method are the choosing of environmental friendly reduction agent, solvent (usually H_2O is preferred) and the non-toxic material as stabilizer[74]. Even, there are some compounds which can be used both as a reductant and a stabilizer, such as glucose and sucrose.

The exploration of another biological (biotemplate) or organic material is very interesting. The biological template includes plant extracts, bacteria, fungi, yeast and algae (Fig. 6). Ag-np which formed from biotemplate is more environmentally benign when used in the medical field because the stabilizer can be easily removed in the body process. This phenomenon leads the Ag-np reaction as a medicine becomes more effective.

Green synthesis by using microorganism: Bacteria can be used as Ag-np template either through intra or extracellular route[72]. The principle of using the bacteria as biotemplate is the role of some bacteria as silver resistant, thus the Ag-np can be accumulated in the bacteria cell wall approximately 25% of

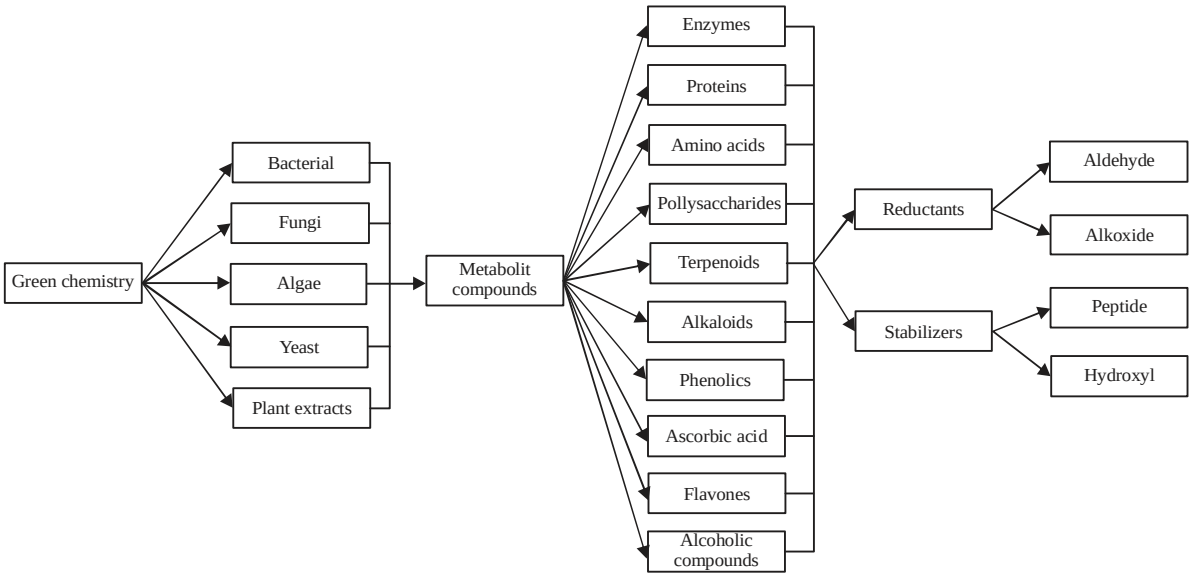

Fig. 6: Scheme of green chemistry for synthesis Ag-np

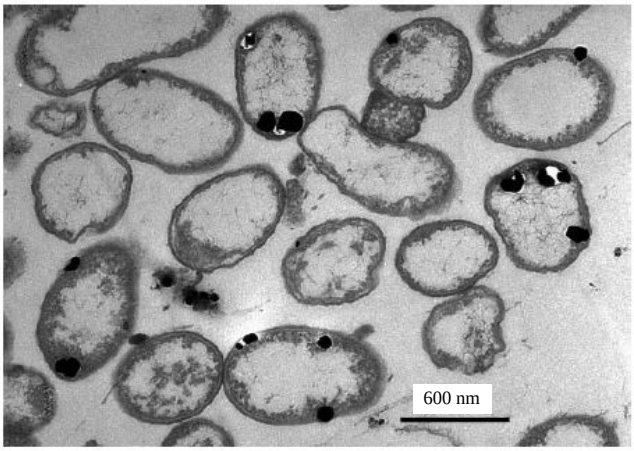

Fig. 7: A TEM Image of *P. stutzeri* AG259 cells. Ag particles are deposited between the cell wall and the plasma membrane[75]

their dry mass. The resistance bacteria produce some reducing compound from their cell, so it can convert silver solution precursor to silver atom or nano-particles.

Klaus *et al.*[75] have prepared silver from *Pseudomonas stutzeri* AG259, a bacterial strain which isolated from silver mining. As a result, the silver particles are large in size (up to 200 nm) and located between the cell wall and the plasma membrane of bacterial *P. stutzeri* AG259 (Fig. 7). The EDX spectrum indicated that the silver content of the product is 90%.

The main drawbacks of using bacteria as nano-particles template are the slow synthesis rate and the limited shapes of the Ag-np compared to the conventional chemical reduction methods. Another drawback is the low yield of nano-particles. For these reasons, fungi-based nano-particles and chemical reaction involving plant-based materials were investigated.

The other extracellular biosynthesis of Ag-np was carried out by using *Trichoderma reesei* (*Hypocrea jecorina*) as fungus biotemplate[76]. The fungus *mycelium* from *T. Reesei* produced enzymes and other metabolites compound such as naphthoquinones and anthraquinones which acted as reductant species. The TEM image showed that the Ag-np was formed with diameter size 5-50 nm. The strong plasmon resonance at 414-420 nm from UV-vis analysis indicated the formation of Ag-np. The advantages of using *T. reesei* compared to other fungus are high production of active enzymes and metabolites, low cost, high growth rate and also easy handling.

Similar to fungi, yeasts were also widely investigated for silver nano-particle synthesis[77-79]. The Ag-np was successfully synthesized from commercial baker yeast, *Saccaromyces cereviceae* via extracellular mechanism[79]. The synthesis was conducted by incubation the mixture of silver nitrate and *S. cereviceae* culture for 1 h at room temperature. The initial yellow color was changed to brown color indicated the formation of Ag-np. As a result, UV-vis spectra showed the Ag-np plasmon resonance at 430 nm. Based on the TEM image, *S. cereviceae* could mediate the Ag-np formation with

60-80 nm in size. The FTIR analysis revealed the presence of protein functional group as the stabilizing agent.

Green synthesis by using plant extracts: The nano-particle preparation by using plants as biotemplate have widely studied. When the metal salt solution is mixed with the plant extracts, the nano-particles are formed within several minutes. The formation of nano-particles by using plant extracts as biotemplate depends on several parameters like the metabolites compound and the concentration of the plant extracts, the pH, the synthesis temperature and the reaction time[80]. Almost all parts of the plants can be used for preparing nano-particles such as leaves, latex, roots, seeds, bark and stem[81]. The advantages of using plants extracts for preparing nano-particles are the plants widely available in every place, safe to handle, environmentally benign and the plants produce a large variety of active agents that can help to reduce metal ions or stabilize the nano-particles[82].

The most important aspect of this method is the active compound of the plants, which make reduction and stabilization process possible. The main active metabolites from plant extracts are biomolecules, such as terpenoids, alkaloids, polysaccharides, enzymes, proteins, flavones, amino acids, alcoholic compounds, phenolics, quinol, linalool, eugenol, methyl chaviol, chlorophyll pigments, caffeine, theophylline, ascorbic acid and other vitamins[83]. The phenolic compounds have hydroxyl and carboxyl functional groups which can make binding to the surface of the metal (as a stabilizer) and also can help to reduce the metal ions. Furthermore, the aldehyde and alkoxide functional groups derived from plants extract metabolites have a strong contribution to reduction mechanism. Both of them serve as an electron donor to the metal salt precursor through nucleophiles addition. This step involved the release of hydride species from the functional group which will reduce the metal cation. While either aldehyde or alkoxide will be oxide become carboxylic acid.

For example, the extracellular synthesis of Ag-np formation was done by using *geranium (Pelargonium graveolens)* leaf extract[84]. The surface plasmon resonance of formed Ag-np occurred at 440 nm. The Ag-np was stable after one-month synthesis. The FTIR spectra showed the significant peak at 1736, 1640 and 1458 cm^{-1}. The broad peak at 1640 cm^{-1} corresponding to the amine band of proteins (chlorophyll) from geranium extracts which capped the particles. The peak at 1736 cm^{-1} corresponding to ester C=O groups of chlorophyll which was involved in the oxidation reduction process. The peak at 1458 cm^{-1} corresponding to stretching vibration of carboxylate ion groups of amino acid. The geranium leaf produced large amount of terpenoids such as citronellol, geraniol and linalool. The terpenoids play important role in reduction process and they were oxidized into carbonyl groups which detected at 1748 cm^{-1}. TEM image revealed that the formed Ag-np was 27 nm in average diameter size, polydispersed and almost spherical in shape.

A summary of recent green chemistry method for preparing the Ag-np is presented in Table 2.

Antibacterial mechanism of Ag-np: Because of the non-harmful and noble metal base, the Ag-np have been investigated for a long time for killing around 650 micro-organisms which cause infections[124]. Nowadays, Ag-np is applied in many antimicrobial applications, includes in the medical field and housewares. The Ag-np is developed in many household products. In the medical application, Ag-np has antiviral activity against HIV-1, the famous viruses which can decrease the body immune[125]. Herein, we review some of the antibacterial research and antibacterial mechanism affected by Ag-np.

The size, structure and shape of Ag-np and also different interaction models between the Ag-np and bacterial are the important issues to investigate. Subsequent, with the small size in nano-particle scale (1-100 nm), the Ag-np provide a large surface area to contact with the bacterial target. As consequence, the physical, chemical and biological properties of Ag-np are very different to the silver bulk[126]. Several mechanisms concerning Ag-np antibacterial action have been proposed by different authors.

Franci *et al.*[126] proposed the possible toxicity of Ag-np. The antibacterial effects of Ag-np due to the activity of the Ag-np and the cationic silver that released from the Ag-np when dissolved in water. The silver ions bound to the protein and nucleic acids of the bacterial cells causing structural damages and deformations of the cell wall. The silver ions would bind with the electron donor functional groups such as phosphates, thiols, hydroxyls, imidazoles and indoles. The Ag-np also damaged the cell wall and induced the released of reactive oxygen species (ROS) which have powerful bacterial action. As a result, ribosomes would be denatured with inhibition of protein synthesis as well as transcription and translation are blocked by binding with the genetic material of bacterial cells (Fig. 8).

Morones *et al.*[127] investigated Ag-np as an antibacterial agent against *P. aeruginosa*, *V. cholera*, *E. coli* and *S. typhus*. The *P. aeruginosa* and *V. cholera* are more resistant than *E. coli* and *S. typhus*. However, when the concentration of Ag-np above 75 μg mL^{-1} there was no significant growth of all bacterial. They proposed three mechanisms of Ag-np toxicity

Table 2: Recent green chemistry methods for preparing Ag-np

Agents	Particle diameter (nm)	References
Bacteria		
Bacillus flexus	12-65	Priyadarshini *et al.*[85]
Bacillus subtillis 10833	30-60	Ghiuta *et al.*[86]
Bacillus amyloliquefaciens 1853	22-90	Ghiuta *et al.*[86]
Streptomyces violaceus MM72	10-60	Sivasankar *et al.*[87]
Chryseobacterium artocarpi	42	Venil *et al.*[88]
Streptomyces griseoplanus	19.5-20.9	Vijayabharathi *et al.*[89]
Fungi and yeast		
Aspergillus tamarii	25-50	Kumar *et al.*[90]
Aspergillus foetidus	20-40	Roy and Das[91]
Macrophomina phaseolina	5-40	Chowdhury *et al.*[92]
Penicillium sps.	75	Shareef *et al.*[93]
Phenerochaete chrysosporium	34-90	Saravanan *et al.*[94]
Penicillium aculeatum Su1	4-50	Ma *et al.*[95]
Cryptococcus laurentii	35-400	Fernandez *et al.*[96]
Rhodotorula glutinis	15-220	Fernandez *et al.*[96]
Algae		
Sargassum muticum	5-15	Azizi *et al.*[97]
Chaetomorpha linum	3-44	Kannan *et al.*[98]
Pterocladia capillacae	7	El-Rafie *et al.*[99]
Jania rubins	12	El-Rafie *et al.*[99]
Ulva faciata	7	El-Rafie *et al.*[99]
Colpmenia sinusa	20	El-Rafie *et al.*[99]
Spirogyra varians	17.6	Salari *et al.*[100]
Gracilaria birdiae	20.2-94.9	De Aragao *et al.*[101]
Plant extract		
Azadirachta indica	34	Ahmed *et al.*[102]
Acorous calamus	31.83	Nakkala *et al.*[103]
Chrysanthemum extract	40-100	Gopinath *et al.*[104]
Thevetia peruviana	10-30	Ghramh *et al.*[105]
Citrus maxima	2-50	Rupiasih *et al.*[106]
Vitis vinifera	30-40	Jha *et al.*[107]
Olive extract	15-30	Khalil *et al.*[108]
Pepper leaf	5-60	Mallikarjuna *et al.*[109]
Ixora coccinea	167.1	Yedurkar *et al.*[110]
Phoenix dactylifera L.	20-60	Aitenneite *et al.*[111]
Malus domestica	145	Umoren *et al.*[112]
Artemisia absinthium	5-20	Ali *et al.*[113]
Viburnum opulus	25	Moldovan *et al.*[114]
Psidium guajava	20-35	Wang *et al.*[115]
Nyctanthes arbortristis	5-20	Gogoi *et al.*[116]
Plumeria alba	36.19	Mata *et al.*[117]
Butea monosperma	20-80	Patra *et al.*[118]
Piper longum	46	Reddy *et al.*[119]
Coffea arabica	20-30	Dhand *et al.*[120]
Diospyros paniculata	17	Rao *et al.*[121]
Heterotheca inuloides	16	Morales-Luckie *et al.*[122]
Lippia citriodora	25	Elemike *et al.*[123]

against the bacterial, especially for Gram-negative bacterials. First, the Ag-np penetrated to the surface of the bacterial cell and broke its proper function, like respiration and permeability. The second, the Ag-np could penetrate cell membrane and caused further damage to the bacterial cell. The Ag-np would bind with sulphur or phosphorus functional group such as DNA, so the Ag-np could disturb the functional metabolism of bacterial. The DNA couldn't do the replication function because of the Ag-np's attack. The third, the Ag-np could release the silver ions which also have great toxicity to the bacterial cell. The silver ions give contribution to inactive the proteins.

Shrivastava *et al.*[128] studied the effect of Ag-np concentration to kill Gram-negative bacterials (*E. coli* and *S. thypi*) and Gram positive bacterial (*S. aureus*). They revealed that Ag-np had major effect to the Gram negative bacterials than the positive ones. When the concentration of Ag-np was 25 μg mL^{-1}, it acted as a strong inhibitor to *E. coli*

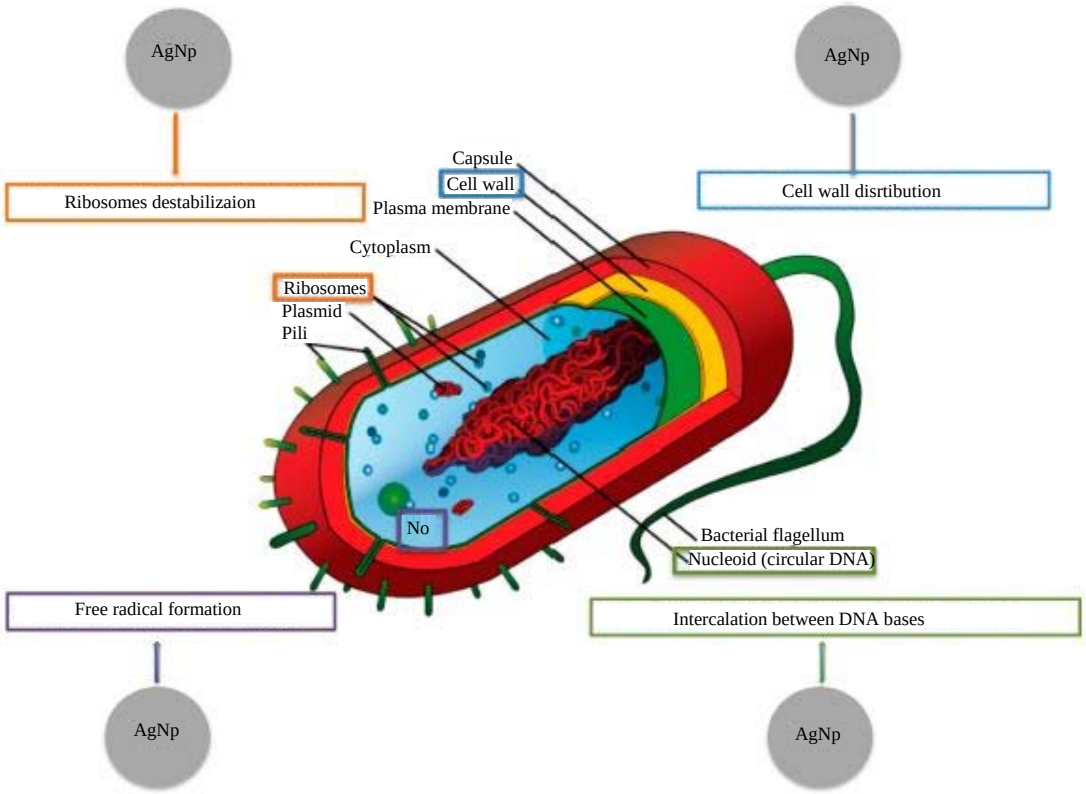

Fig. 8: Mechanism of Ag-np toxicity[126]

and *S. thypi* growth. Whereas, that concentration gave less effect to *S. aureus*. The Gram-negative bacterial have a layer of lipopolysaccharide at the exterior, followed by a thin layer of peptidoglycan (7-8 nm). The lipopolysaccharide was weak strength and lack rigidity. Vice versa, the Gram-positive bacterial have a thick layer of peptidoglycan (20-80 nm) and have rigid structure due to the linear polysaccharide chains cross-linked by short peptides to make three-dimensional structure.

Antimicrobial effects of Ag-np depend on some factors, such as size, environmental condition (pH and ionic strength) and the stabilizing agent[129]. In the form of the silver element, it is inert but on coming in contact with water, it releases silver ions[130]. The silver ions prefer interact with the nucleosides rather than the phosphate groups of nucleic acids. Thus, all forms of silver or silver-containing compounds which have antimicrobial activity are in the form of silver ions (Ag^+)[131,132].

The similar theory was revealed by Lansdown[132]. It proposed that silver was inert and exhibited no biocidal action in its metallic form, but, silver could ionize in the presence of water or tissue fluids to release silver ions. These ions showed a strong affinity for sulfhydryl groups and protein residues on cell membranes. The mechanism could be described as follows:

The silver ions bound to electron donor receptors such as amino, imidazole, disulfide, phosphate and carbonyl on cell membranes via intracellular absorption by phagocytosis and endocytic vacuoles. The inactivation process of enzyme membranes like phosphomannose isomerase caused denaturation of the bacterial cell. This phenomenon could disturb its functional capacity to regulate the diffusion of nutrients (such as phosphates and succinates) and inhibited the effusion of essential metabolites and electrolytes. The predominant intracellular effect of silver due to its ability to impair key intracellular enzyme systems by impairing trace metals and electrolytes leading to defective respiratory pathways and RNA-DNA replication[133]. There were some kinds of literature showing the electrostatic attraction between positively charged Ag-np and negatively charged bacterial cells[134] and many researchers suggested that Ag-np is the most suitable bactericidal agent[135].

Figure 9 represents the ability of Ag-np in inhibiting the growth of *S. aureus*. Figure 9a shows the culture of *S. aureus* before being treated and Fig. 9b showed the culture after

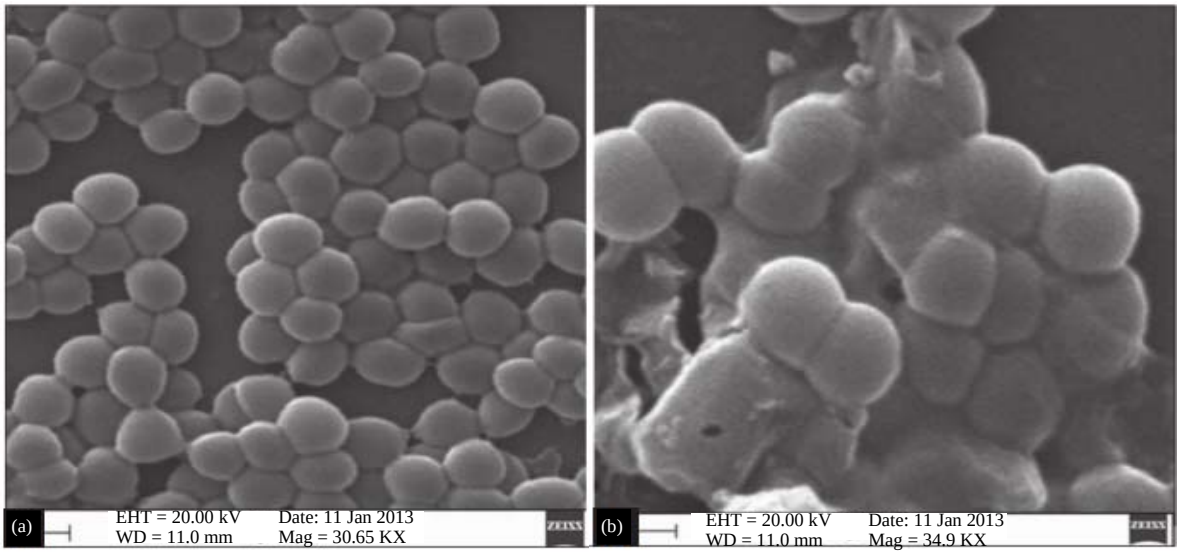

Fig. 9(a-b): SEM images of *S. aureus* biofilms after 24 h of incubation (a) Untreated and (b) Treated with Ag-np[136] 20 μg mL^{-1}

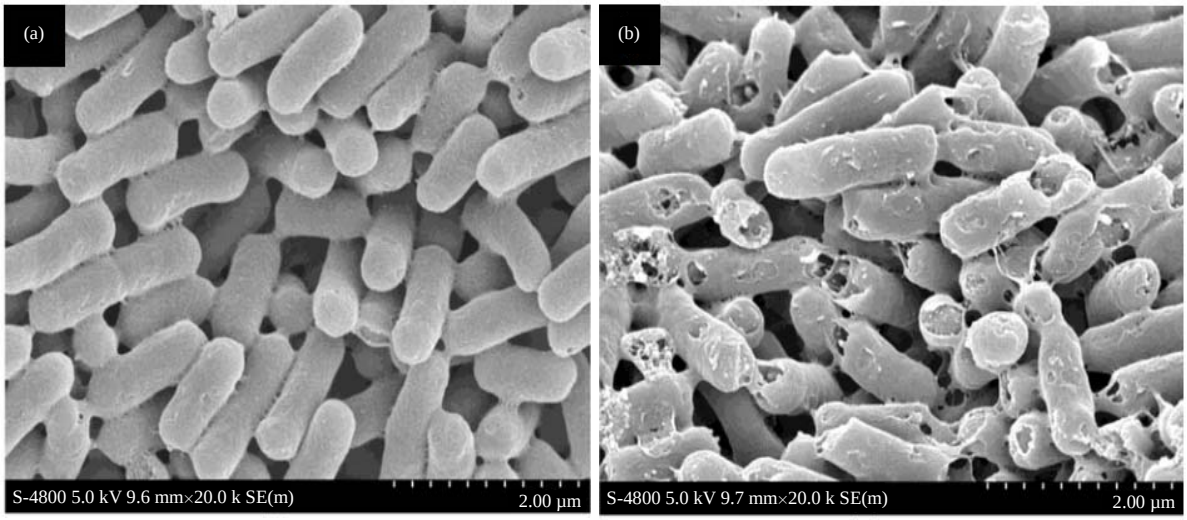

Fig. 10(a-b): SEM micrograph of *E. coli* (a) Before and (b) After treatment with Ag-np[137]

being treated with (20 μg mL^{-1}) Ag-np. In the beginning, *S. aureus* cultures had normal cell morphology with smooth cell surface. But with the Ag-np treatment there is a change in bacterial morphology. Ag-np appears to inhibit bacterial colonization on the surface. The SEM results clearly showed that the bacterial substrate treated with Ag-np does not allow for bacterial colonization and biofilm formation when compared to the control without Ag-np treatment. Figure 9b also clearly shows some damage to *S. aureus* cells[136].

A destruction evidence of *E. coli* cells due to the effect of Ag-np was also presented by Zhang *et al.*[136]. The SEM images were used to evaluate the morphology of untreated and treated *E. coli* in LB medium. The surface of *E. coli* cells untreated with Ag-np was smooth and had a rod shape. However, after *E. coli* treated with Ag-np, the SEM image showed that the *E. coli* surface had serious damage. Many rod cells show 'big holes' on their cell walls, while others are even fragmented and mis-shaped (Fig. 10).

Gram-positive bacteria are less susceptible to Ag^+ than Gram-negative bacteria. This phenomenon is generated by the Gram-positive bacterial cell wall made up of peptidoglycan molecules and has more peptidoglycan than Gram-negative bacteria. The decreased liability of gram positive bacteria can also simply be explained by the fact

that the cell wall of Gram-positive bacteria is thicker than that of Gram-negative bacteria[137]. It is why the Ag-np is easier to attack Gram-negative bacterial than the Gram-positive bacterial.

CONCLUSION

Some general routes to synthesize Ag-np are physical, chemical reduction and green chemistry methods. Among of the synthesis methods, the green chemistry method is the most promising method due to its simplicity and environmentally benign. For the biomedical application, Ag-np has been reported to have a good inhibitory effect against both Gram-positive and Gram-negative. As an antimicrobial agent, effects of Ag-np toxicity are influenced by both of Ag-np and also the silver ions which released during contact with water or tissue fluid. The Ag-np can damage the cell wall and induced the released of reactive oxygen species (ROS) or radical species which have powerful bacterial action.

SIGNIFICANCE STATEMENTS

The information about various synthesis procedures and the antimicrobial properties of silver nano-particle (Ag-np) can give the significant impact for both of material science and biochemistry field. The authors proposed that green chemistry is the most promising method for preparing silver nano-particle compared to others due to its easy preparation and environmentally benign. Furthermore, the wide availability of biological precursor leads the development of green chemistry technology. Although Ag-np has a good inhibitory effect both against Gram-positive and Gram-negative bacteria, the new understanding shows that the Gram-positive bacteria are more susceptible to Ag-np than Gram-negative bacteria.

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