Silver nano solution, manufacturing methods, characteristics and applicability

ABSTRACT

The development of human society is associated with the development of materials through the ages: stone, copper, iron, polymers and now nanomaterials. With extremely small sizes, very large surface areas and quantum effects of nanomaterials, it offers many outstanding properties and opens up many special applications.Silver nanomaterials (AgNPs) have both the properties of metallic silver while expanding and adding new properties, so the application scope is also more developed, especially in the fields of environment, medicine and health protection for humans. Nanosilver is also prepared according to the principle of "top-down" from metal or "bottom-up" from ion by physical, chemical, physicochemical or biological techniques or a mixture of combinations. The obtained nanosilver product is a true colloidal solution whose properties are very dependent on the preparation methods, but the basic properties are such as the nature of the plasmonic surface resonance of silver nanoparticles by UV-Vis, particle shape, size and structure by TEM, SEM, AFM, FTIR, XPS, XRD, nanoparticle and colloidal size distribution by Laser Scattering Particle Size Distribution Analyzer and Zeta Phoremeter Instrumentation. The concentration of nano silver is usually determined by methods AAS, ICP-MS, ICP-OES. Depending on the intended use in the fields of: catalysis, photovoltaic, microelectronics, environment, medicine, health, etc., methods to determine the corresponding properties are also applied. Because AgNPS has many special characteristics, the most prominent is the field of killing many bacteria and viruses to protect the environment and human health, the AgNPS development research strategy is specially noticed in many countries in the worlds. Research is very focused on precise control of concentration, particle size, purity, use of environmentally friendly materials and lower costs as well as increasing efficiency and safety in biological water treatment applications. activity, diagnosis and treatment in medicine.

Keywords: *AgNPs, methods, characteristics, applicability.*

1. INTRODUCTION

Metallic silver was discovered thousands of years BC and became a very precious metal used as currency in feudal society in many countries as well as jewelry and household items.[1] With properties good conductor of electricity, heat, light sensitivity and antiseptic, silver has been used in the fields of electricity, electronics, film and medicine since very early. Since the development of nanomaterials with effects on subatomic small size, large area and quantum,[2,3] silver nanomaterials (AgPNs) have also been focused on researching innovations such as:[4,5] electrical properties,[6] electronic,[7] catalytic,[8] and especially antibacterial.[9-11] Because AgNPs have many applications in science, technology and life, especially with very good antibacterial ability,[12-14] so many research and manufacturing methods such as physics,[15-17] biology,[18-20] chemistry,[21-23] and electrochemistry[24-27] have focused their research.

2. MANUFACTORING METHODS

2.1. Physical Methods

2.1.1. The principle of "Top - down"

Fabrication of AgNPs by physical method also follows the “top-down” principle with bulk metallic silver using a large amount of heat to separate the silver into vapor and then condense it like PVD,[28,29] or granular and then dispersed. such as laser cutting[30,31] or electric arc.[32,33] Figure 1 shows the principle of laser method (a)[30] and arc discharge (b)[33] along with corresponding TEM images of the obtained AgNPs particle size and shape and size.

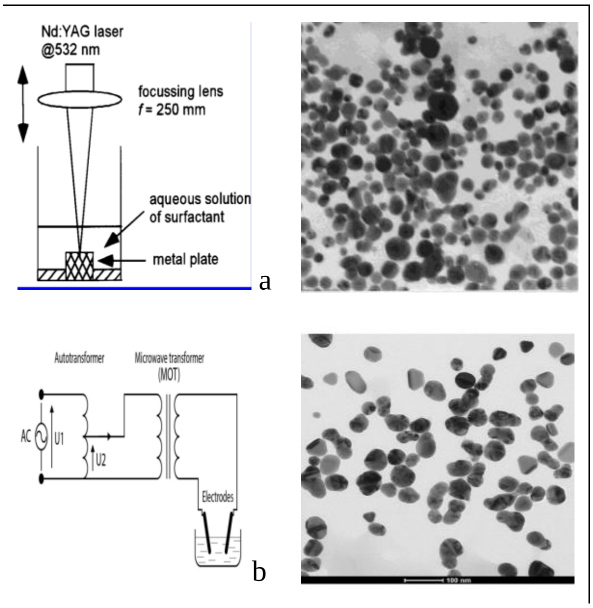


Figure 1. Schematic diagram and TEM image of AgNPs, a) Laser method, b) arc discharge method

The AgNPs solution obtained by the above methods has a time-dependent light to dark yellow color and has a characteristic UV-Vis spectrum from 400 to 404 nm. Figure 1 shows that the shape of the nanoparticles is not uniform, so the particle size distribution spectrum is wide from 10 to 300 nm and the average is 46.8 to 48.9 nm. The zeta potential values from -20.4 to -22.31 mV show that AgNPs colloidal solutions can be prepared by physical methods without the need for stable stabilizers. Although the production of AgNPs by the above physical methods does not use chemicals, so it has high purity, but the equipment is complicated, uses a lot of energy, the concentration is not high and the quantity obtained is not large. Therefore, the cost is high and the field of use is limited.

2.1.2. The principle of "Bottom - up"

Physical methods can also implement the principle of preparing AgNPs from the “bottom-up” by beams: gamma,[34-37] electrons,[38] or microwave[39] activating components in solution to reduce Ag^+ of $AgNO_3$ salts into AgNPs.

According to the author group Bui Duy Du[40], the energy of gamma rays can affect the components of the medium such as water to form strong reactive agents including strong reducing agents such as H- radical with potential value - 2, 3 V:

$$H_2O \xrightarrow{\gamma-\text{radiation}} e^-_{aq},\ H^\bullet,\ OH^\bullet,\ H_2O_2,\ H_2,\ H_3O^+, \ldots s \qquad (1)$$

$$Ag^+ + H^\bullet \rightarrow Ag^0 + H^+ \qquad (2)$$

$$nAg^0 \rightarrow AgNPs \qquad (3)$$

Although the obtained AgNPs have the best shape and small size, the fabrication process must use different stabilizers[34-37,40,41] and the maximum value of the UV-Vis spectrum ranges from 405.5 to 41.8 nm. With the advantage of using available equipment, the process of technology is not complicated and can prepare a large amount of AgNPS solution, so the cost will be more reasonable, but the resulting solution still has a large amount of NO_3^- ions. As well as other stabilizers and by-products, the field of application is only suitable for environmental remediation.

2.2. Chemical Methods

2.2.1. Reducing agents

The chemical method for preparing AgNPs solution is to implement the “Bottom-up” principle to create nanoparticles from Ag^+ ions of silver salts by reduction process.[42] The commonly used silver salt is $AgNO_3$ and the reducing agents used are very different. such as glucose,[43,44] sucrose,[45] hydrazine,[46-48] ethylene glucol, ethanol, aniline,[49] citrate,[46,50-54] hydrogen,[52] borhidird[53]

The chemical method of preparing AgNPS solution is to follow the principle from the “Bottom-up” to create nanoparticles from the Ag^+ ions of silver salts by reducing the reduction process.[42] The commonly used silver salts are $AgNO_3$ and the reducing agents that have been used very different such as glucose ($C_6H_{12}O_6$),[43,44] sacarose ($C_{12}H_{22}O_{11}$),[45] hydrazine (N_2H_4),[46-48] ethylene glycol ($C_2H_6O_2$), ethanol (C_2H_5OH), aniline ($C_6H_5NH_2$),[49] sodium citrat ($Na_3C_6H_5O_7$),[46,50-53] hydrogen (H_2),[52] sodium borhydird ($NaBH_4$)[53-57] ...

Table 1 presents the reaction equation to form AgNPS with a number of different reducers. To ensure the reduction process is completely done, the reducing agent usually has many times compared to silver salt. From the reactions in Table 1 can be seen: In addition to the spherical silver nanoparticles after the reaction, there are ions of silver salt such as NO_3^-, Na^+, the products of reducing agents and stabilizers are added. Removing these ingredients to get AgNPS is completely pure, expensive and also changes the properties of AgNPS, so the product is usually applied only in areas that do not require AgNPS high purity.

Table 1 also shows that nanoparticles are obtained as a wide area, so it is necessary to use stabilizers to control the size of nanoparticles as desired. From Table 1, the reducing reaction mechanism according to different authors[54-58] is also different. It also means that the substances in AgNPS solution after the reaction will also vary, for example, $NaBH_4$ reduction reaction (10) creating B_2H_6[54-57] gas will escape from the solution and if the reaction (11) quantity H_2 gas from the solution will be 3.5 times higher than (10).[58].

Table 1. Reducing and reactions to create AgNPS

Reducing agent	Reaction equation	Size, nm	Ref
$C_6H_{12}O_6$	$C_6H_{12}O_6+2Ag^+ + 2OH^- \rightarrow 2Ag^0+C_6H_{12}O_7+H_2O$ (4)	20.80 sphere	44
N_2H_4	$4AgNO_3+N_2H_4+4NaOH \rightarrow 4Ag^0+N_2+4NaNO_3+ 4H_2O$ (5)		48
N_2H_4	$4AgNO_3 + N_2H_4 \rightarrow 4Ag^0+N_2+4HNO_3$ (6)	8-50 sphere	46
RCHO	$2AgNO_3+RCHO+2NaOH \rightarrow 2Ag^0+RCOOH+ 2NaNO_3 +H_2O$ (7)	10-250	49
$C_6H_5NH_2$	$C_6H_5NH_2+AgNO_3 \rightarrow Ag^0+ C_6H_5NH_2NO_3$ (8)	10-30	49
$C_6H_5O_7Na_3$	$4AgNO_3+C_6H_5O_7Na_3+2H_2O \rightarrow 4Ag^0+C_6H_8O_7+ 3NaNO_3+ HNO_3 +O_2$ (9)		50
$NaBH_4$	$AgNO_3 + NaBH_4 \rightarrow Ag^0 +1/2H_2 +1/2B_2H_6 +NaNO_3$ (10)	10-80	54-57
$NaBH_4$	$AgNO_3 + NaBH_4 + 3H_2O \rightarrow Ag^0+7/2H_2 + B(OH)_3 + NaNO_3$ (11)	30-40	58

2.2.2. Stabilizers

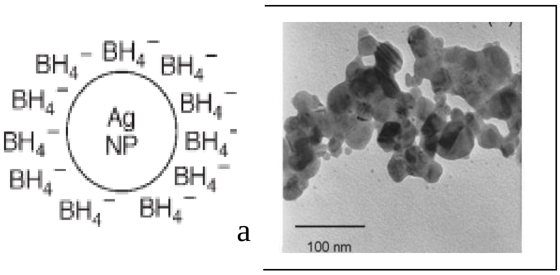
The process of creating a silver nano colloidal solution with reducing agents that always exists in the system with ions and reducing agents, so silver colloids can be formed according to the equation:

$$2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O \quad (12)$$

$$Ag_2O + R\text{-}CHO \rightarrow 2Ag^0 + R\text{-}COOH \quad (13)$$

$$nAg^+ + nNaBH_4 \rightarrow nAg^0(BH_4^-)_x + nNa^+ \quad (14)$$

and simulated as shown in Figure 2.[44,54]



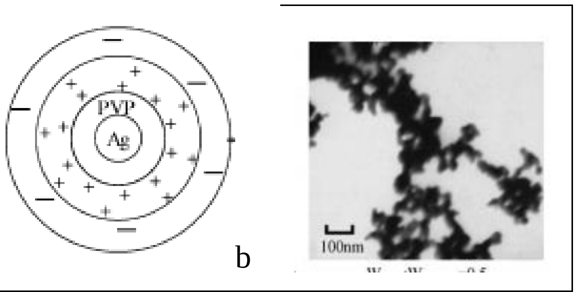
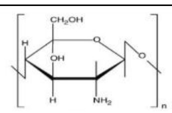
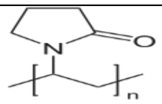
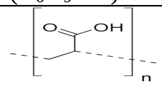
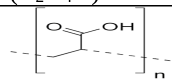
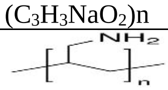
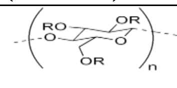
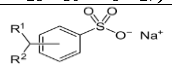
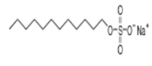
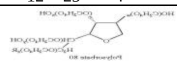
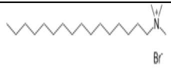
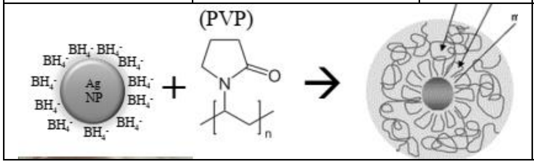


Figure 2. AgNPS colloidal seeds and stamp images are made up of $AgNO_3$ chemical reduction with reducing agents: a) $NaBH_4$, b) R-HO with PVP.

In order to control the size and shape of AgNPS in the colloidal solution, it is not formed into a large particles, stabilizers are high molecular compounds or surfactants added to the chemical reaction.[59-61] Stabilizers often have functional groups, dissolve well in the reaction environment, good compatibility or high biological activity, non-toxic and biodegradable ability.[62] Table 2 presentation of some stabilizera often used for chemical manufactoring of AgNPS such as: Chitosan,[62-67] PVA,[68,69] PVP,[51,59,70] ...

Table 2. Stabilizers are often used in the process of chemical manufactoring of AgNPS.

Stabilizers	Chemical formula	M_{ever}, g/mol	Ref.
Chitosan poly β(1,4)D-glucosamine cation		3,800-20,000	66
PVP polyvinyl-pyrrolindone	 $(C_6H_9NO)n$	40,000	59
PVA poly vinyl alcohol	 $(C_2H_4O)n$	85.000	
PAA polyarcrylic acid	 $(C_3H_3NaO_2)n$	15,000	
PAH poly allylamine hydrochloride	 $(C_3H_8ClN)n$	15,000	
CMC carboxymethyl cellulose	 $C_{28}H_{30}Na_8O_{27})n$	90,000	
NaDDBS Surfactnts (anion)	 $C_{18}H_{29}SO$ Na	348	
SDS Surfactants (anion)	 $C_{12}H_{25}SO_4Na$	288	
TW80 Surfactants		1,310	

(neutral)	$C_6H_{124}O_{26}$		
CTAB Surfactans (cation)	 $C_{19}H_{42}BrN$	365	
			

From Table 2, stabilizers can be found with electrical charge groups of straight or cyclic circuits, that can orient the adsorption on the AgNPS core to form a micell or reverse micell with the corresponding charge to combat flocculation of the colloidal system.[71,72] So that the stabilizers with the appropriate nature and concentration will control the size and shape of the AgNPS colloid as well as the characteristics of AgNPS as desired.

2.2.3. Silver nanocomposite

Fabrication of silver nanocomposite with chemical reducing processes will diversify AgNPS carried materials for applications in life. Composite materials carried AgPNs are usually studied as polymers PP, PET, Nylon, PC, ABS,[73,74] PU,[75] PE,[76] ceramic, pottery,[77-79] glass,[80] fabric, fiber,[81-83] paint.[84-85] Common manufacturing methods are dispersed AgNPs made by chemical methods in materials, but can also be made *in-situ* from $AgNO_3$ with reducing agents in the material during the processing ceramics, fabric or polymers.[86-88]

2.3. Biological method

2.3.1. Microorganism

The biology method uses bacterial microorganisms, yeast, mushrooms, molds as $AgNO_3$ silver-deducted agents into metal silver and AgNPS.[89-91] microorganisms using silver salts as nutrients to survive and develop as described in Figure 3.

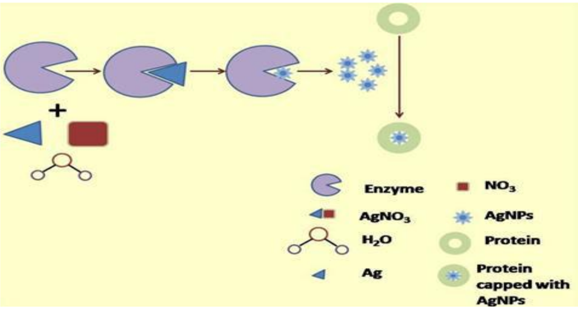


Figure 3. Microorganisms use Ag^+ as a nutrient and reduce it to AgNPs.

From Figure 3 it can be seen that the protein can act as a stabilizer to control the size of AgNPs. There are many types of microorganisms studied and used to make AgNPs from $AgNO_3$ which are presented in Table 3.

Table 3. Particle size, characteristic UV-Vis spectra and references of some typical microorganisms using AgNPs preparation.

Microorganism	Size/UV, nm	Ref.
Enterobacteria	52.5 / 420-430	92
Rhodopseudomonas palustris	5-20 / 420-460	93
Rhodobacter Sphaeroides	9.56 / 420	94
vibrio alginolyticus	75 / 420	95, 96
Halococcus salifodinae BK6	50.3 / 380-440	97
Bacillus	42-94 / 450	98
Euplotes focardii	20-70 / 420	99
Haloferax	27.7 / 458	100
Verticillium (fungus)	25 / 420	101
Aspergillus fumigatus	5-25 / 420	102
Penicilium	5-25 / 430	103

The results from Table 3 show that microorganisms can also reduce $AgNO_3$ salts to AgNPs with characteristic UV-Vis wavelengths from 380 to 460 nm and average particle sizes less than 100 nm. The special thing is that AgNPs products are stabilized with stable proteins for more than 6 months, so there is no need for stabilizers. However, the ions of $AgNO_3$ salt are still present in the reaction product, so the purity of AgNPs is not enough for application in the field of medicine.

2.3.2. Extraction solution – green chemistry

Humans develop in association with the plant environment and often use many types of plants for food or medicine, so using plants in the preparation of AgNPs is also a method with many advantages in terms of extremely rich raw materials, environmentally friendly and low cost. Therefore, the method of preparing AgNPs by plant extracts has been studied all over the world such as USA,[104] China,[105] India,[106] Germany,[107] Africa[108] and Vietnam.[109] Water extracted from parts of plants such as leaves,[110] roots,[111] bark,[112] tubers,[113] flowers,[114] fruits[115] can all be used to prepare AgNPs. Table 4 presents extracts of some plants used to prepare AgNPs. Using plant water extract as $AgNO_3$ reducing agent to prepare AgNPS does not need to use more stabilizers, but the product is still available with NO_3^- ions and reducing products, so it also limits the application field.

Table 4. Extracts of some plants used to prepare $AgNO_3$.

The plants	Science name	Part	Ref.
Geraniums	*pelargonium graveolens*	Flower	104
Cordyceps	*Cordyceps militaris*	Total	105
Mud	*Brillantaisia patula, Crossopteryx febrifuga and Senna siamea*	Tree and leaves	108
Soybean	*soymida febrifuga*	Total	110
Carrot	*D. carota*	Tubers	111
Dill	*Syzygium cumini*	Total	112
Turmeric	*Curcuma Longa*	Tubers	113
Hibiscus	*Hibiscus Rosa*	Flower	114
Papaya	*Papaya*	Fruit	115
Basil	*Ocimum santum*	Total	117
Ginger	*Zingiber oficinale*	Total	123
Tea	*Camellia sinensis*	Leaf	125
Sinus	*Azadirachta indica*	Leaf	124
Sesame oil (castor oil)	*Jatropha curcas*	Total	126
Euphorbiaceae	*Acalypha Indica*	Total	135
Mint	*Mentha piperita*	Total	122
Chrysanthemum	*Stevia rebaudiana*	Total	134
Amaranthaceae	*Chenopodium album*	Total	120
Fabaceae	*Casia fistula*	Total	133
Terminalia	*Terminallia chebula*	Leaf	118
Cinnamon, Camphor	*Cinnamomum camphora zeylanicum*	Bark	121
Garlic	*Allium sativum*	Total	127
Curry patta	*Murraya koenigii*	Leaf	132
Lemon basil	*Coleus amboinicus*	Total	131
Alfalfa	*Medicago sativa*	Total	130
Oranges, Lemons	*Citrus sinensis*	Total	128
Lemongrass	*Lemon grass*	Total	119
Bình bát	*Coccinia grandis*	Leaf	129
Combretaceae	*Terminalia catappa*	Leaf	128
Aloe vera	*Aloe vera*	Leaf	116
Lime tree	*Robustra*	Leaf	109

From Table 4, it can be seen that plants from all continents of the world are food sources, spices such as oranges, lemons, papayas, sesame, basil to pharmaceuticals such as cinnamon, garlic, lemongrass, and cordyceps as well as wood-bearing trees such as neem tree, neem tree, etc., can be extracted using water containing $AgNO_3$ desalting agents into AgNPs. Common reducing agents in plant extracts are flavonoids, terpenoids, polyphenols, alkaloids, glucose which are compounds having carbonyl and hydroxyl groups or amine groups.[136]

2.4. Electrochemical Method

2.4.1. With electrolyte

The electrochemical method in the field of Chemistry-Physics can perform a top-down process by oxidizing the metal silver anode in the electrolyte into Ag+ ions with electrode potential value +0.799 V:[137]

$$Ag - e \rightarrow Ag^{+} \qquad (15).$$

Simultaneously combined with the cathode reaction to reduce silver ions from the electrolyte to form silver nanoparticles, performing the bottom-up process: [138-142]

$$Ag^{+} + e \rightarrow Ag^{0} \qquad (16)$$

$$nAg^{0} \rightarrow AgNPs \qquad (17).$$

It is also possible to perform the preparation of AgNPs by simply reducing the reaction on the cathode (16) with $AgNO_3$ salt dissolved in the electrolyte solution and an inert anode such as Pt.[143,144] To control the size of AgNPs obtained at the cathode can be used electrochemical specifications such as voltage, current density, conductivity as well as supporting measures such as pulses, vibrations, ultrasound or even strong escape gas on the electrode with higher voltages than normal water dissociation. With the usual electrochemical method, the electrolyte or anion NO_3^- of $AgNO_3$ still exists in AgNPS products, so it also limits the application field.

2.4.2. With high voltage

Electrode reactions can occur in a non-electrolyte medium such as double distilled water with very low conductivity but the voltage must be sufficiently high[138,139,141] or very high.[145-149] There are two typical electrode arrangements in the electrochemical reactor when using high voltage (Figure 4).

With high DC voltage the potential drop across the electrodes will still be greater than the decomposition potential of water as well as the equilibrium electrode potential of Ag and the electrochemical oxidation on the anode to form Ag^{+} ions as the reaction (15) as well as water is electrochemically decomposed to form O_2:

$$2H_2O - 4e \rightarrow O_2 + 4H^{+} \qquad (18).$$

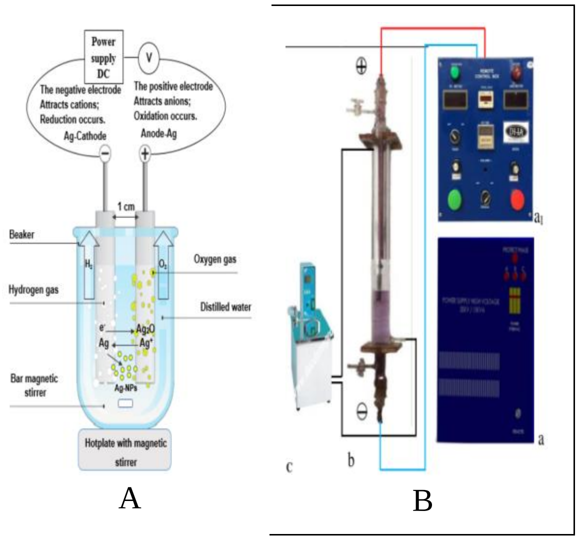


Figure 4. A) the cathode is parallel to the anode,[140] B) the bottom cathode is far from the upper anode146-[148]

At the same time on the cathode, the water will also be decomposed to form H_2 gas that escapes strongly towards the anode as shown in Figure 4B:

$$2H_2O + 4e \rightarrow H_2 + 2OH^{-} \qquad (19).$$

Due to the strong escaping gas covering the cathode surface, the amount of Ag^{+} ions generated from the anode moves slowly due to poor conductivity, so it is difficult to reach the cathode to carry out the reaction (16). Therefore, the reduction of Ag^{+} to Ag^{0} and then to AgNPs according to (17) will be carried out by nascent H_2 gas from the cathode and dispersed into the solution:

$$2Ag^{+} + H_2 \rightarrow 2Ag^{0} \qquad (20).$$

Figure 5 shows the process of generating AgNPs by H_2 generated from the cathode by electrochemical reaction from high voltage. Figure 5a shows that the color of distilled water is transparent, but after 3 minutes of reaction, H_2 gas escaping from the cathode turned white (b), and after 15 minutes of reaction, AgNPs formed turned dark color from the cathode side (c) and after 30 min the color of AgNPs occupied the entire reaction vessel (d).

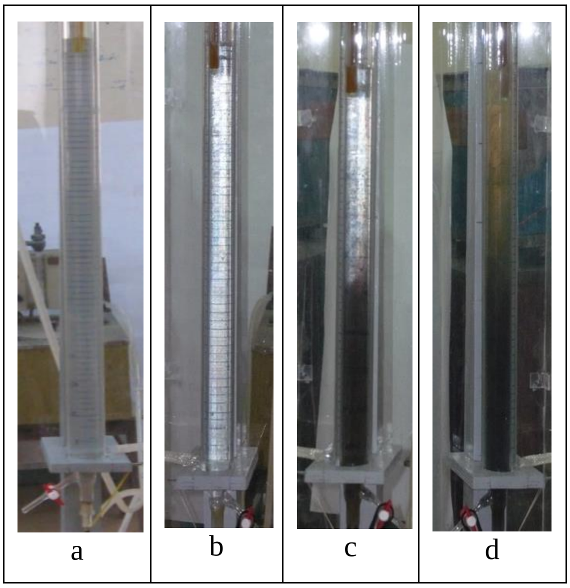


Figure 5. AgNPs generation process by high voltage electrochemical reaction.

With the method of electrochemical manufactoring AgNPS by high voltage DC in distilled water with Ag electrode, the obtained product still has a spherical shape, size smaller than 100 nm with UV-Vis spectrum at about 420 nm and the ability to kill all kinds of bacteria very good. However, the zeta potential is opposite in sign to the chemical method and has a high value, so there is practically no need to use a stabilizer. The conductivity of colloidal solutions is very small because there are no ions of the reactants so the high purity is suitable for applications where only AgNPs are required.

2.5. Plasma method

Plasma is the fourth state of matter, the ionized state is changed from a gaseous state when further energized.[150] Unlike high-temperature plasma which produces a fully ionized state with only electrons and ions, low-temperature plasma ionization process only partially contains not only electrons, ions but also atoms, neutral molecules and radicals and is being applied in many fields of science, technology and life.[151] The cold plasma state is also used for the preparation of AgNPs by the reduction of $AgNO_3$ by free electrons or hydrogen atoms generated by plasma according to the reaction (16) or (20).[152-154] Figure 6 shows the plasma generation methods for the preparation of AgNPs.[152,153,155]

From Figure 6 it is shown that the gaseous medium can be used either by air on the surface (Figure 6A,b) or by blowing air between the two electrodes (Figure 6A,c; 6B) or by the ARC arc generating steam (Figure 6C).

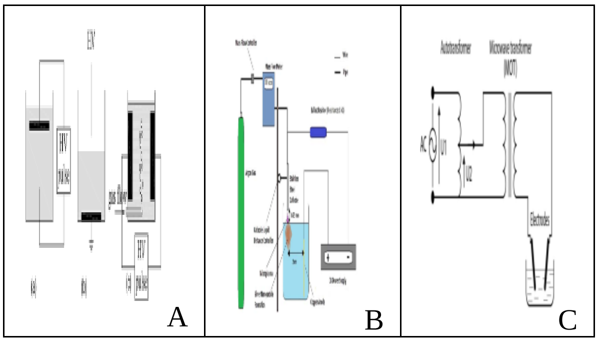


Figure 6. Principle of plasma generation for the preparation of AgNPs.

The plasma generation process uses electrodes and electrochemical reactions to create a gaseous environment when the electrodes are arranged as shown in Figures 4B and 5 or Figure 6A,a, so the plasma method can also be considered as an electrochemical method with high voltage. High. In the plasma state, the water will be decomposed on the electrodes to create a large amount of gas that does not obey Faraday's electrochemical theorem as well as ionization reactions to create atoms, molecules and radicals:

On the cathode: $2H_2O \rightarrow 2H_2 + O_2$ (21)

On the anode: $4H_2O \rightarrow O_2 + 3H_2 + H_2O_2$ (22)

$$H_2O + e \rightarrow H^\bullet + OH^\bullet \quad (23)$$

$$H^\bullet + H^\bullet \rightarrow 2H \quad (24)$$

$$OH^\bullet + OH^\bullet \rightarrow 2H_2O + 2O \quad (25)$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \quad (26)$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \quad (27)$$

$$H_2O + e \rightarrow H_2O^\bullet \quad (28)$$

$$H_2O^\bullet + H_2O \rightarrow H_2O + H^\bullet + OH^\bullet \quad (29)$$

$$H_2O^\bullet + H_2O \rightarrow H_2 + O^\bullet + H_2O \quad (30)$$

$$H_2O^\bullet + H_2O \rightarrow 2H^\bullet + O^\bullet + H_2O \quad (31).$$

UV rays in the presence of plasma also contribute to the radical reaction:

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \quad (32).$$

The reactants generated from the plasma medium can participate in the formation of AgNPs in addition to the reactions (16) and (20):

$$2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O \quad (33)$$

$$2Ag^+ + O_2 \rightarrow Ag_2O_2 \quad (34)$$

$$Ag_2O + H_2 \rightarrow 2Ag^0 + H_2O \quad (35)$$

$$Ag_2O + H_2O_2 \rightarrow 2Ag^0 + H_2O + O_2 \quad (36)$$

$$Ag_2O + H_2O_2 \rightarrow Ag_2O_2 + H_2O \quad (37)$$

$$Ag_2O_2 + 2H_2 \rightarrow 2Ag^0 + 2H_2O \quad (38).$$

Figure 7 presents the process of generating AgNPs by high-voltage DC with the contribution of electrochemical plasma, showing that after the time of gas generation from the electrochemical reaction (Figure 7a), an anodic electrochemical plasma will appear after 15 minutes (Figure 7b) and the light yellow AgNPs color appearing from the anode towards the cathode gradually darkens over time of 23, 26, 35 min, respectively with Figures 7c, 7d and 7e.

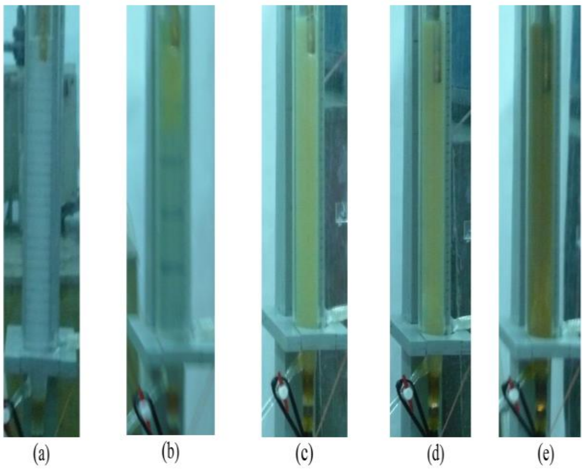


Figure 7. The process of generating AgNPs by high voltage DC with the contribution of electrochemical plasma.

The process of creating Ag_2O and Ag_2O_2 intermediates besides Ag^0 due to the presence of O_2, OH^-, $OH^{\bullet}$, H_2O_2 agents, etc. in the electrochemical plasma environment has created a yellow color before turning black.[156] By Ronghen, EDX and XPS spectra also demonstrated the presence of O in AgNPs accounting for 5.77 ÷ 9.6% and also increased the bactericidal efficiency of AgNPs.[157-160] Similar to the method of preparing AgNPs by High voltage DC, electrochemical plasma contribution will create the ability to increase the speed, product concentration as well as the ability to kill bacteria, although there is a small amount of Ag_2O or Ag_2O_2, but it does not affect the purity of the product.

3. CHARACTERISTICS OF NANOSILVER

3.1. Silver nanoparticles

The characteristics of shape and size of AgNPs were determined by imaging methods by electron microscopy SEM, TEM, FE-TEM. Particle size distribution was determined by statistical particle counting software from SEM or by Laser Scattering Particle Size Distribution Analyzer. Figure 8 presents TEM images of AgNPs shape and size (a) as well as particle size distribution from TEM (b) and laser determination (c). Figure 8 shows that AgNPs prepared by different methods all have near-spherical shape but different sizes in the nanometer region with Gaussian distribution as determined by laser method.[154,158,161]

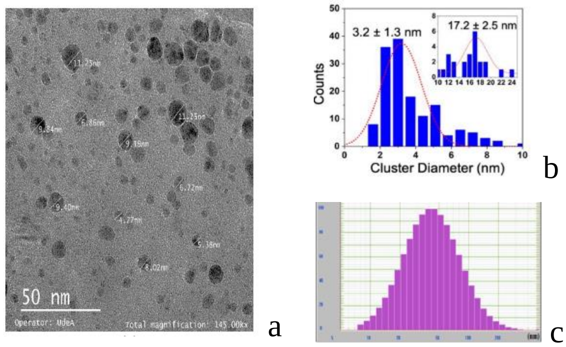


Figure 8. TEM image of AgNPs (a) and particle size distribution counted from TEM image (b) and laser particle size distribution analysis (c).

X-Ray,[162] XRD,[153] XPS[142,152] methods are also used to further investigate the properties of AgNPS particles in terms of phase, ratio of elements or ions: Ag/Ag^+/O, contributing to a better understanding of state of AgNPs in solution.

3.2. Nano silver colloid solution

3.2.1. Color

Figure 9 presents AgNPs products prepared by different methods such as: a) chemical,[54,163] or b) plasma.[155]

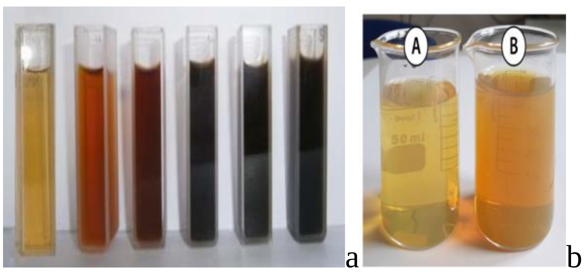


Figure 9. Color of AgNPs colloid a) chemically prepared, b) by plasma at different times and concentrations.

The AgNPs products obtained are all true solutions in the state of a transparent colloidal system with color from light yellow to brown or black depending on the concentration and preparation time, while the colorless solution will have no AgNPs.[163]

3.2.2. UV-Vis and zeta potential

The AgNPs colloidal solution has the important properties of UV-Vis plasmon spectrum and zeta potential. Figure 10 shows the UV-Vis spectrum,[164] zeta potential and colloidal particle distribution.[155]

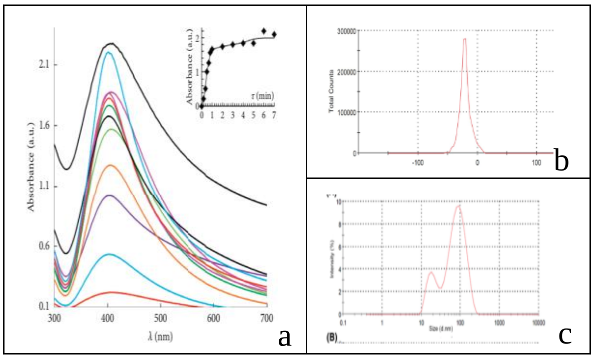


Figure 10. UV-Vis spectrum (a), zeta potential (b) and colloidal particle size distribution (c) of AgNPs colloidal solution.

From Figure 10a, the UV-Vis spectrum can be found of the AgNPS glue solution that has a range of 400 nm and increases the height when the concentration or reaction time increases and the location is moved when the acacia grain nature is essentially. affected. Figure 10b shows that the Zeta value is about -22.31 mV that proves that the surface of the AgNPS acacia seeds is positive and the size of colloidal seeds distributed from 20 to 90 nm (Figure 10c). Therefore, Zeta is the diffusion layer, the surface of the glue seeds should be dependent on the environment and charge of the AgNPS seed surface with values that change from yin and yang, but the absolute value is greater than 20 MV, the glue system will be durable over time. Table 5 presents the zeta value of AgNPS glue solutions with different stabilizers.[60,66,139,159]

Table 5. The zeta value of some stabilizers.

Stabilizer	Chemical formula	mW, g/mol	ζ, mV
NaDDBS	$C_{18}H_{29}SO_3Na$	348	5÷ -30
SDS	$C_{12}H_{25}SO_4Na$	288	-2÷ -20
TW80	$C_{64}H_{12}4O_{26}$	1310	4÷ -15
CTAB	$C_{19}H_{42}BrN$	365	20÷ -30
PVP	$(C_6H_9NO)n$	40000	0÷ -25
PAA	$(C_3H_3NaO_2)n$	14000	5÷ - 25
PAH	$(C_3H_8ClN)n$	15000	5÷ 20
CMC	$(C_{28}H_{30}Na_8O_{27})$	90000	0÷ -10
Chitosan	$(C_6H_{11}NO_4)n$	20000	50 ÷ 70
PP SH[165]	*Entada spiralis*	Chiết	-80,7
PPĐH[139]	DC 25 kV	Ag	-(27÷39)
PPPL[159]	ARC discharge	Ag	-(40÷70)

Table 5 shows that the value of zeta is very dependent on the nature of stabilization of chemical structure, weight, electronegativity,[66,67] as well as depending on the modulation method and composition of ions that exist in glue solution.

3.2.3. Conductivity and pH

Because Ag^0 or AgNPS silver particles are dispersed in water environments, it is impossible to conduct electronic conduct as metal as well as ionic forms like electrolyte solution. However, while using $AgNO_3$ in the methods as well as reducing the ionic amount of: NO_3^- as well as the reducing agent: Na^+ or the products of the reducing agent will create the conductivity of the AgNPS solution. Moreover, AgNPS colloidal seeds also adsorb ion and create charge, although not large and much but also create conductivity. Table 6 The conductivity and pH of AgNPS glue solutions are prepared from different methods.

Table 6. Electrical conductivity (χ, mS/cm) and pH of AgNPS solution are prepared by chemical and electrochemical methods

Chem	*c*, ppm	RO	100	200	300	500
	χ, mS/cm	0,01	0,27	0,36	0,46	0,58
	pH	6,9	4,6	4,9	4,4	4,5
Electr	*c*, ppm	NC	109	185	285	411
	χ, mS/cm	0,003	0,08	0,07	0,07	0,07
	pH	6,9	6,64	5,63	5,78	5,79

Table 6 also shows that with the methods using of $AgNO_3$, conductivity levels increases when the concentration increases but the methods of electrochemical or plasma use the silver electrode, the conductivity is small and has almost no change, even when the synthesis time as well as when the concentration increases.[166]

3.2.4. Concentration of AgNPS

Determining the concentration of AgNPS is not as simple as determining the concentration of soluble substances because it is difficult to separate between silver nano and ionic. With AgNPs synthesis methods by using $AgNO_3$ often think that the process of reaction completely and the AgNPS concentration is also considered as $AgNO_3$ concentration. The AAS method transfers AgNPs to Ag^+ so it cannot be determined by the nano form. With the methods of using Ag metal, it is possible to determine by soluble silver weight ($c_{\Delta m}$) with the assumption that silver is soluble for formation of AgNPs.[167] It can also determine the amount of AgNPS by adjectives The amount of electricity according to the law of Faraday ($c_{Far.}$), but besides the dissolving process, there are other electrochemical processes, so the concentration of Faraday's law is usually larger than the amount of soluble metal ($c_{Far.} > c_{\Delta m}$).[139] The AAS method can also be used to determine the AgNPs concentration of the electrochemical and plasma modulation methods, but it cannot be separated from Ag^+. The UV-Vis spectroscopic method for the determination of AgNPs alone would be the most accurate, but standard curve construction is not feasible because standard solutions are difficult to obtain.

3.3. Antibacterial ability

3.3.1. Traditional

Since BC, silver's bactericidal properties have been used for prevention and treatment of diseases such as: acupuncture needles, containers for liquids and drinking water for the prevention and treatment of infections. Former feudal dynasties in many countries around the world used spoons, knives, bowls and plates in eating and drinking to kill pathogens to ensure life safety. Silver has also been used for a long time in dentistry, to treat neurological diseases, eye diseases, to treat wounds, and to disinfect drinking water systems. During the World Wars, colloidal silver was used to fight gastrointestinal diseases and infections. From the late 19th century to the present, colloidal silver has been used quite widely in the form of oral and injectable drugs to treat arthritis, bronchitis, respiratory, lung, influenza as well as gastrointestinal diseases, stomach ulcers or Disinfection of purulent-necrotic burn wounds, dermatosis, boils or even syphilis, mastitis, meningoencephalitis, vestibular...[168]

3.3.2. Outstanding antibacterial properties

Elemental silver has outstanding bactericidal ability because Ag^+ ions exist in the form of salt.[163] In the form of AgNPs, with extremely large contact area, it is easy to provide Ag^+, so the bactericidal efficiency is improved many times. Although there is still no consensus, but the bactericidal mechanism of Ag^+ is agreed with 3 possibilities: (1) Destruction of the function of the cell wall; (2) Destruction of respiratory function due to inactivation of -SH group in O_2 transporter; (3) Destruction of DNA function by dimerization of pyridine interferes with DNA replication of bacterial cells. In addition, atomic oxygen is produced from the reaction:

$$2Ag^+ + O^{2-} \rightarrow 2Ag^0 + O^0 \qquad (39)$$

It also inhibits the growth of bacteria. Furthermore, the plasmons of AgNPs are susceptible to thermogenesis and destruction of bacteria. Because of many different ways to kill bacteria, the bactericidal ability of AgNPs cannot be greasy or resistant like current antibiotics.

3.3.3. Kills many types of bacteria

Unlike antibiotics that are only suitable for bacteria, AgNPs can kill up to 650 types of bacteria, gram negative and positive as well as viruses and fungi, mold.[168-170] Recent studies have shown AgNPs have remarkable anti-inflammatory and antiviral potential, even against viruses such as HIV[171,172] or Sars corona,[173,174] Monkeypox,[175] Hepatitis B,[176] Syncytial,[177] Herpes,[178] Tacaribe,[179] West Nile, Hanta, Nipah, Hendra, Chikugunya, as well as viruses of avian origin and pig.[173,180]

3.3.4. Toxicity

The toxicity of silver and silver ions has been of concern for a long time due to the phenomenon of blue skin when the amount of silver accumulates and has not been eliminated in time.[180] With its small size, it is dispersed in gaseous and liquid environments and solids when used, AgNPs also easily penetrate into the body and accumulate in cells through the respiratory tract,[181] esophagus or skin contact.[182] Therefore, the toxicity of AgNPs is also very noticeable.[183,184] Although AgNPs are not as toxic as ions, AgNPs still generate ions[185] from AgNPs and accumulate in organs such as lungs,[186] liver, and spleen[187] and cause harmful effects depending on the time and concentration of exposure[188] as well as the size. and the shape of AgNPs.[189]

4. APPLICATIONS

4.1. In chemistry

Silver metal as well as nanosilver are applied due to its properties such as absorption and optical control, bactericidal, electrical and thermal conductivity, and especially as a catalyst for some reactions as well as as a sensor in analysis in chemistry.[190]

4.1.1. Catalysis

The reduction of oxygen of epoxides to alkenes catalyzed by AgNPs can be as efficient as 99% as efficient as using Au or AuNPs.[191] AgNPs are used as catalysts for the reduction reactions of nitro aromatic compound,[192] carbonyl as well as oxidation of alcohols, silanes, olefins, alkylation of amines and arenes as well as ring-opening or closing reactions and a variety of value reactions.[193] AgNPs are used as homogeneous or heterogeneous catalysts. to synthesize many special chemical compounds with high efficiency such as:[194] pyrimido 96%, triazole 98%, pyrano 96%, isoxazole 93%, quinoline 88%, tetrazole 93%, benzopyranopyrimidine 95%, bivalent amine 92% , etc...

4.1.2. Analysis

Silver nanomaterials with advantages in size, shape and surface also play an important role in determining and controlling electrical, optical, physical and especially chemical properties. With the GC electrode combined with AgNPs, it is possible to have excellent electrocatalytic activation as a sensor for determining H_2O_2 in water with a concentration of 0.92 µM.[195] With different techniques, it is possible to fabricate the mounted electrode. AgNPs for performing cyclic voltammetry CV, differential voltammetry DPV, linear sweep voltammetry LSV, square wave voltammetry SWV analyzes with up to the limit of ppb detection of various organic compounds.[196] Especially, has advantages in detecting chemical contamination in the state of the environment, so the number of publications by 2022 is increasing rapidly.[197]

4.2. In environmental treatment

The excellent bactericidal ability of AgNPs has been applied to environmental treatment mainly in 3 directions: Surface disinfection, water disinfection and air sterilization.[198]

4.2.1. Contact surface

Contact with material surfaces is the most frequent activity, so the antibacterial properties of AgNPs are also studied for applications in construction materials, fabrics or plastic tools. Interior paints with additive AgNPs 0.1 ÷ 0.5 ppm have good antibacterial effect.[199] Glass surface coated with AgNPs not only has bactericidal value but also has plasmon effect to increase absorption capacity. energy.[200] Plastic coated with AgNPs has many useful applications in medical transmission materials, in food packaging and preservation,[201-203] as well as export tropical fruits.[204-206] Fabric fibers surface coated with AgNPs with the amount of 180 mg/kg have a bactericidal effect of 99.28%, even after 30 washing cycles it is still 98.77%.[207]

4.2.2. Water treatment

Water is necessary for the life of all things. Humans also use water for all living activities as well as production, so they need clean water but it is easy to pollute water sources with different wastes.[208] AgNPs with special chemical and biological properties should be noticed. It is intended for use in environmental treatment systems including water.[209] The European Union alone uses up to 20.5 tons of AgNPs to treat wastewater each year.[210] Effects of AgNPs in water treatment Not only in the ability to kill bacteria but also in the chemical reaction ability[211] as well as sensor application to control water pollution.[212] In aquaculture, seafood AgNPs have also been used in water treatment to reduce pollution. infection as well as prevention of network diseases have high economic efficiency.[213-215]

4.2.3. Air handling

The excellent bactericidal effect of AgNPs has also been studied for application to air purification. By depositing AgNPs into a porous quartz tube fitted with an air purifier with a capacity of 250 m^3/h, it is possible to both process organic compounds up to 91.6% butanol, 80%% acetone, and 70.1%. diethyl ether and 43% benzene as well as 99% bacteria and fungi and installed for E Hanoi hospital.[216] The air conditioning system combined with AgNPs due to improved heat transfer ability saved energy on average 36- 58%.[217] However, when using AgNPs to treat air pollution, great care must be taken to limit the dispersion of AgNPs into the air so as not to cause inflammation of the respiratory system.[218] Therefore, the concentration of AgNPs to spray in Air should also be kept to a low level and avoid long exposure times.[219]

4.3. Nanomedicine

AgNPs are widely used in many biomedical applications, known as nanomedicine including diagnostics, therapeutics, drug manufacturing, medical device coating, and personal healthcare. With increasing applications in medicine, a better understanding of the mechanisms is becoming necessary.[220]

4.3.1. Disinfectant

Because the hospital environment needs to be clean, the special antibacterial ability of AgNPs is noticed as a disinfectant agent for the environment as well as tools. The MBC concentration of AgNPs for hospital bacterial strains such as S. Aureus or P. Aeruginosa in the operating room after 20 minutes is 100 µg/mL and after 24 hours it is 12.5 µg/mL.[221]

Fluid pathways or medical instruments are also tested for emergency disinfection with AgNPs.[201] Even the air in hospital rooms can be treated with contamination by bacteria as well as organic substances with AgNPs.[215]

4.3.2. Diagnose

Silver nanoparticles are used in imaging diagnosis and treatment of dental and oral cancers, acting as a carrier to disperse to targets along with chemotherapy agents and as radiation and phototherapy enhancers. motion. It is valuable for studying inflammation, tumors, immune responses, and the effects of stem cell therapy, in which contrast agents are conjugated or surface-modified and bioconjugated to particles. nano. Silver has an important role in imaging systems with plasmonic properties that should produce a clearer image.[222,223] Due to reactive oxygen species (ROS) of cancer cells AgNPs control and damage DNA. contribute to the formation of cancer nano flavor in nano medicine.[224.225]

4.3.3. Healing

The advantage of AgNPs is that they can kill many types of bacteria[171-180] and are not resistant to drugs like antibiotics,[226] so special attention is paid to exploiting them to treat diseases. Disinfecting all types of open wounds[227] especially in the treatment of burns[228] or teeth and mouth[229] with AgNPs not only heals the wound quickly but also leaves almost no scars after healing. With infectious diseases such as HIV, hepatitis, SARC, and chickenpox, injections with a concentration of 20 ppm of 10 nm AgNPs have achieved good curative effects.[230] Because cancer is currently an incurable disease, AgNPs have also been researched and applied and found that cancer cells have been inhibited by AgNPs from proliferating as well as angiogenesis due to the destruction of living and proliferation conditions.[231] Furthermore, AgNPS particles have the ability to absorb heat, so they can use energy from the laser source to kill cancer cells.[232]

5. CONCLUSION

Nano silver is prepared by chemical, physical, biological and physicochemical methods. Raw materials for the preparation process are $AgNO_3$ salt and reducing chemicals such as $NaBH_4$, citrate salt, plant water as well as reducing microorganisms, or activating rays that create reducing properties of the solution such as γ. It is also possible to use Ag to disperse by laser or dissolve the anode into ions and then reduce it to form AgNPs. The appropriate purity for different practical applications of AgNPs products depends on the method and materials used. Pure AgNPs solution is prepared by high-voltage electrochemical method or electrochemical plasma method because it only uses Ag and distilled water.

The basic characteristic of AgNPS is that the nanoparticle has a nearly spherical shape, the size is in the nanometer range and the UV-Vis spectrum is in the range of 420 nm with the height depending on the concentration and the pH value depending on the size. The zeta potential has an absolute value of $\geq$ 20 mV, which characterizes the stability of the silver nano colloid solution, then the negative or positive value depends on the method and the composition of ions in the solution. Pure AgNPs colloidal solution has a very small electrical conductivity, but the conductivity value will increase depending on the concentration of reducing agent ions or reaction products in the solution. A very important characteristic of AgNPs is the ability to kill microorganisms from positive and negative bacteria, viruses to fungus by destroying cell membranes, affecting -SH groups as well as destroying functions microbial DNA.

AgNPs are applied in chemical fields as catalysts and analytical sensors. In the environment, AgNPs are applied to treat bacterial infections as well as air and water pollution. In medicine, AgNPS is given special attention in research and application to: treat environmental infections, medical tools and equipment; diagnose and heal many diseases, including dangerous diseases such as, burn, HIV, SARC and cancer.

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