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A review of Silver Nanoparticles - Research Trends, Global Consumption, Synthesis, Properties and Future Challenges

Hadi Nur, *Universiti Teknologi Malaysia*
Achmad Syafiuddin, *University Technology Malaysia*
Salmiati Salmiati, *University Technology Malaysia*

Review

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A Review of Silver Nanoparticles: Research Trends, Global Consumption, Synthesis, Properties, and Future Challenges

Achmad Syafiuddin,[a] Salmiati,[a,b]* Mohd Razman Salim,[a,b] Ahmad Beng Hong Kueh,[c] Tony Hadibarata[d] and Hadi Nur[e,f]

[a]*Department of Environmental Engineering, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Johor, Malaysia*
[b]*Centre for Environmental Sustainability and Water Security (IPASA), Research Institute for Sustainable Environment (RISE), Universiti Teknologi Malaysia, Johor, Malaysia*
[c]*Construction Research Centre (CRC), Institute for Smart Infrastructure and Innovative Construction (ISIIC), Faculty of Civil Engineering, Universiti Teknologi Malaysia, Johor, Malaysia*
[d]*Department of Environmental Engineering, Faculty of Engineering and Science, Curtin University, Sarawak, Malaysia*
[e]*Center for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, Johor, Malaysia*
[f]*Central Laboratory of Minerals and Advanced Materials, Faculty of Mathematics and Natural Science, State University of Malang, East Java, Indonesia*

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Silver nanoparticles (AgNPs) are intensively investigated for their superior physical, chemical, and biological properties. A proper knowledge of these properties is essential to maximizing the potential applications of AgNPs in several areas while minimizing their risks to humans and the environment. This paper aims to critically review AgNPs from the perspectives of research trends, global consumption, synthesis, properties, and future challenges. Generally, AgNPs can be synthesized using three methods, namely physical, chemical, and biological, and the related works as well as their numerous advantages and disadvantages are presented in this review. In addition, AgNPs can be potentially explored for various applications. Future challenges on (AgNP) synthesis, their release into the environment, and scaling up production, as presented in the review, suggest that several potential topics for future works are available to promote a safer and more efficient use of these nanoparticles. Studies on AgNPs in Malaysia have increased since the Malaysian government officially established a directorate for nanotechnology development. This calls for a proper set of policies on AgNPs starting from their production to utilization as well as their effects on various related industries and the environment.

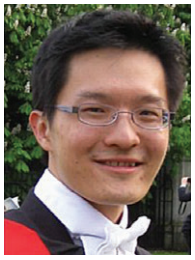
Keywords: Silver nanoparticles; Nanomaterials; Nanotechnology; Environmental chemistry.

Achmad Syafiuddin *received the B.Sc. degree from the Department of Physics (theoretical physics division), Bogor Agricultural University, Indonesia, in 2014, and the M.Phil. degree from Universiti Teknologi Malaysia (UTM), Malaysia, in 2016. Currently, he is working toward the Ph.D. degree under the supervision of Dr. Salmiati and Dr. Tony Hadibarata at the Department of Environmental Engineering, UTM. His research interests include numerical analysis and physical chemistry, specifically the evaluation of the fate and transport mechanisms of silver nanoparticles in the water environment.*

*Corresponding author. Email: salmiati@utm.my

Salmiati *obtained the B.Sc. degree in biological science from Syiah Kuala University, Indonesia, the Master of Environmental Engineering and Ph.D. degrees from Universiti Teknologi Malaysia (UTM), Malaysia. Currently, she is a Senior Lecturer with the Department of Environmental Engineering and Centre for Environmental Sustainability and Water Security (IPASA), UTM. She research interests include environmental microbiology, environmental chemistry, biotechnology, and bioremediation.*

Mohd Razman Salim *received the B.Sc., M. Sc., and Ph.D. degrees from Brighton Polytechnic, UK, North Carolina State University, USA, and the University of Newcastle, UK, respectively. Currently, he is a full Professor with the Department of Environmental Engineering, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Malaysia. His research interests include advanced water and wastewater treatment, industrial and hazardous waste treatment, and environmental monitoring.*



Ahmad Beng Hong Kueh *received the B.Eng. degree from the Faculty of Civil Engineering, Universiti Teknologi Malaysia, Malaysia (UTM), and the Ph.D. degree from the Engineering Department, University of Cambridge, UK. He is currently a Research Fellow and Senior Lecturer with the Construction Research Centre, Faculty of Civil Engineering, UTM. His current research interests include thermo-mechanics and advanced applications of lightweight fiber-reinforced composites under static and impact loads by means of both numerical and experimental approaches. He is also interested in multi-disciplinary research covering steel and concrete structures, in particular their bonding, connection, and bracing behaviors under mechanical and fire loadings. He has also published works on natural nanomaterials, weak soil geoengineering, biomagnetic behaviors of blood flow, as well as hydro and environmental engineering matters, employing various measurement techniques as well as finiteelement, finite difference, and meshfree modeling methods.. Dr. Kueh presently serves on the editorial board of the* Malaysian Journal of Civil Engineering.

Tony Hadibarata *obtained the B.Sc. degree from Mulawarman University, Indonesia, in 2001, and the M.Sc. (environmental chemistry microbiology) and Ph.D. degrees from Ehime University, Japan, in 2006 and 2009, respectively. He is now an Associate Professor with the Department of Environmental Engineering, Faculty of Engineering and Science, Curtin University, Malaysia. His research interests include environmental engineering, environmental chemistry, applied microbiology, enzyme technology, biodegradation, and bioremediation.*

Hadi Nur *obtained the B.S. and M.Eng. (cum laude) degrees in 1992 and 1995, respectively, and the Ph.D. degree (zeolite chemistry) from the Universiti Teknologi, Malaysia (UTM), in 1998. He worked for 1 year as a UTM Postdoctoral Fellow and 2 years as a Japan Society for Promotion of Science (JSPS) Postdoctoral Fellow at the Catalysis Research Center (CRC), Hokkaido University, Japan. He continued his research there at the Center of Excellence (COE), HU, as a Visiting Researcher. In May 2002, he joined UTM. He was a Visiting Scientist at the Institute for Heterogeneous Materials Systems, Helmholtz-Zentrum Berlin for Materials and Energy, Germany, from July to September 2015. Currently, he is a Full Professor and an Adjunct Professor with UTM and State University of Malang, respectively.*

INTRODUCTION

Silver nanoparticles (AgNPs) are a class of materials with sizes in the range 1–100 nm. The interest in the study of AgNPs with respect to their various different behaviors has recently increased because of their unique and attractive physical, chemical, and biological properties.[1–7] AgNPs are also known to have unique properties in terms of toxicity, surface plasmon resonance, and electrical resistance. Based on these, intensive works have been conducted to investigate their properties and potential applications for several purposes such as antimicrobial agents in wound dressings, anticancer agents, electronic devices, and water treatment.[8–14]

Although it has been reported that AgNPs have toxic properties that can inhibit bacterial growth, are hazardous to zebrafish and the human reproductive system, and are lethal to cell-based *in vitro* systems, they are still abundantly utilized in several commercial products such as contraceptive devices and feminine hygiene products.[15–19] Because of such health concerns, a number of researchers have recently carried out measurements and reported that several consumer products released AgNPs into the environment in large amounts.[20] Washing machines were found to release AgNPs into the environment at an average concentration of 11 μg/L.[21] In another study, AgNPs were found to be released from outdoor facades to the environment during the initial runoff events with a maximum concentration of 145 μg/L.[22] The aforementioned events raise potential environmental and health alerts since the toxicity threat of AgNPs can be observed near the vicinity of consumers, particularly in the freshwater ecosystem.

There are several review papers published to address the issues associated with AgNPs in terms of their toxicology properties during their use as antimicrobial agents for textiles, dental biomaterials, and biodetectors, as well as during their syntheses.[23–40] For instance, toxicity properties including cytotoxicity and genotoxicity of capped or uncapped AgNPs have been reviewed in detail.[37] Their toxicity mechanisms after oral exposure were also thoroughly discussed.[41] In addition, a recent review of AgNPs had focused on their synthesis using plant extracts for antimicrobial applications.[42] The majority of the aforementioned reviews focus chiefly on the minor-scale synthesis of AgNPs. The issues during the scaling up of AgNP synthesis are somewhat absent from these papers, although this information is highly beneficial for industrial-level production. Therefore, this paper aims to address this gap, starting from their global usage and research trends to future challenges including issues regarding their release to the environment and scaled-up synthesis procedure. In addition, a case study on the utilization of AgNPs in Malaysia, which has not been reviewed elsewhere, is covered.

The contents of this paper can be briefly presented as follows. A review of the research trend is first offered. Global consumption of AgNPs is then presented. Although AgNP synthetic procedures have been widely reviewed, we report an updated discussion on their existing physical, chemical, and biological synthestic approaches. It is then followed by a description on their properties such as morphology and size, crystalline structures, toxicity as well as optical, thermal, electrical, and catalytic properties. The review continues with future challenges of AgNPs in terms of synthesis procedure, issues regarding their release into the environment, and scaled-up fabrication, which are new to this review. Also, a case study of AgNP utilization in Malaysia is highlighted. This specific section details on the nanotechnology development, research trends, applications, and policy urgency.

RESEARCH TRENDS

The increased popularity of research on AgNPs in the past decades is strongly evident from Figure 1, which highlights the related works that use "silver nanoparticle" as keyword.[43] It is a clear proof that studies on AgNPs are interesting and being continually pursued even today. In the first 20 decades, studies on AgNPs were more focused on synthesizing and characterizing them using chemical approaches. Physical and biological approaches were further proposed because of their safe and green nature. Today, many works are concentrated on biological procedures and applications for several purposes.

Specifically, subject area, source title, country, and affiliation of AgNP publications are also depicted in Figure 1. It is worth noting in Figure 1 that materials science is the dominant subject area of AgNPs. In addition, the *Journal of Nanoparticle Research* has published more topics on AgNPs than others. The top six

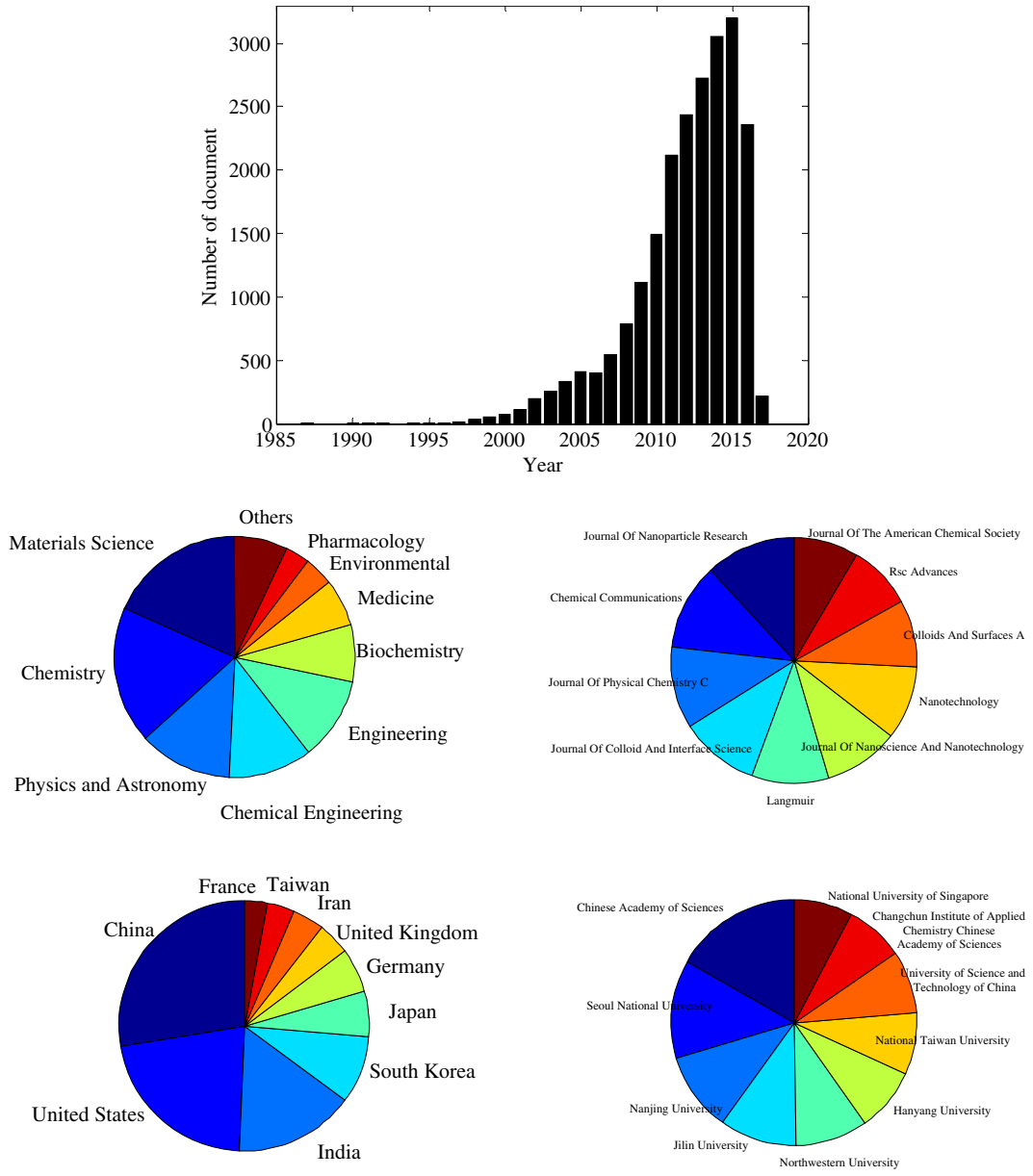


Fig. 1. Publications identified via keywords "silver nanoparticle" from 1987 to January 2017.[43]

institutions that have published on this topic are the Chinese Academy of Sciences, Seoul National University, Nanjing University, Jilin University, Northwestern University, and Hanyang University. Furthermore, China, the United States, India, South Korea, Japan, and Germany are the top six countries active in publishing works on AgNPs.

It is interesting to see that publications on AgNPs is generally dominated by the developed countries. Besides the studies on AgNPs, the development of nanotechnology is widely explored in and originate from these countries. This trend is closely associated with their national income, intellectual property policies, and human resources. India and China are the two developing countries that have shown recently activity in developing nanotechnology. In this regard, the Department of Science and Technology, India, has invested $20 million for nanomaterials science and technology development.[44] China ranks the third in the number of nanotechnology patent applications filed. Furthermore, it is important to note that nanotechnology development can be achieved through

Table 1. Worldwide silver nanoparticle suppliers[45]

Company name	Size (nm)	Phase	Specification
ABC Nanotech	15–35	Suspension	Dispersed in alcohol; solid content <10 wt%
Applied Nanotech Holdings	45	Powder	P (>99%)
Auto Fibre Craft	30–54	Powder	Dry, uncoated, pure powder silver in elemental form
Chengdu Alpha Nano Technology	30–50	Powder	P (>99.9%) w/0.3% PVP
Cline Scientific	30	Suspension	Citrate stabilized in Milli-Q, spherical
EPRUI	20–80	Powder	P (99%); spherical
Inframat Advanced Materials LLC	127	Powder	P (99.95%)
IoLiTec	35	Powder	P (99.5%)
Kemix	90	Powder	P (>99.9%)
Microspheres-Nanospheres	2–250	Suspension	Spherical sizes available from 2 to 250 nm
MKnano	90	Powder	P (99.9%)
MTI Corporation	55	Powder	
NaBond	25	Powder	P (>99.9%)
Nano Ocean Tech	6	Powder	Surface ligand dodecanethiol
Nano Technology Inc.	127	Powder	Spherical
NanoComposix, Inc.	10–127	Suspension	Monodisperse
Nanocs	30	Suspension	In aqueous, 0.01% Ag
Nanogap	25–45	Powder	P (85%)
Nanostructured & Amorphous Materials, Inc.	90–210	Powder	P (99%) metal basis, spherical, cubic structure
NanoXpert	20	Suspension	
NovaCentrix	25	Powder	
NTbase	80	Powder	P (99.99%) spherical
Particular GmbH	5–10	Suspension	Pure nanoparticle dispersions from laser ablation
PlasmaChem GmbH	20	Suspension	Colloidal suspension 0.5 mg/mL
PNF	70	Powder	P (99.9%)
QuantumSphere, Inc.	22–190	Powder	
Seashell Technology, LLC	50–127		Spherical
Shanghai Huzheng Nano Technology	15	Powder	P (99.99%)
Sisco Research Laboratories	90	Powder	P (>99.9%)
SkySpring Nanomaterials	50–60	Powder	P (99.95%) spherical
Stanford Advanced Materials	50	Powder	P (99.9%) nearly spherical
Strem Chemicals, Inc.	50–70	Suspension	In water
Sukgyung	20–30	Suspension	Solvent: water
Sunano	35	Powder	P (>99.8%)

knowledge transfer by means of research collaboration and international funding. Also, serious awareness and close involvement of the national government are essential.

GLOBAL CONSUMPTION

Global consumption of AgNPs is predicted to increase owing to their increasing industrial demand. Table 1 lists the main worldwide AgNP suppliers.[45] Intensive use in various industries such as electronics, appliances, textiles, and medical applications is due to their remarkable properties and behaviors compared to other nanomaterials. Moreover, recent literature reports that AgNPs can be easily synthesized at room temperature using physical, chemical, or biological procedures. Their characterization has been well established using various methods. Also, their behavior has been simulated and verified using experimental data.

Figure 2 shows the global consumption of AgNPs in various applications as reported by Grand View Research, Inc.[46] It is obvious from the figure that healthcare is the largest consumer of all. Also, healthcare shows the fastest growing trend compared to other applications. Increasing demand for antibacterial and antifungal

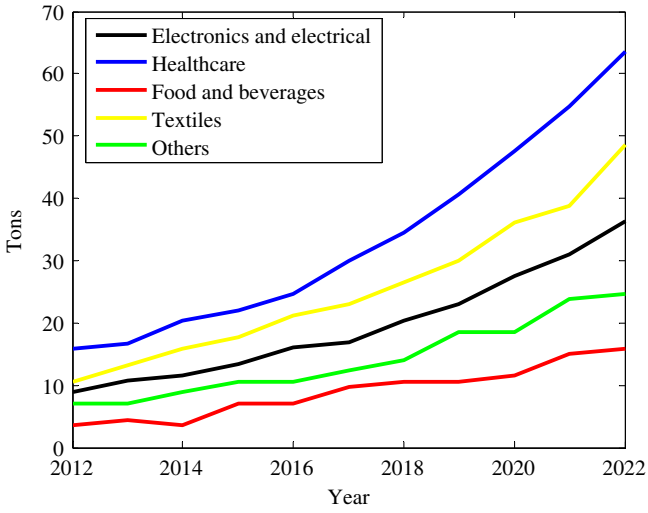


Fig. 2. Global consumption of silver nanoparticles.[46]

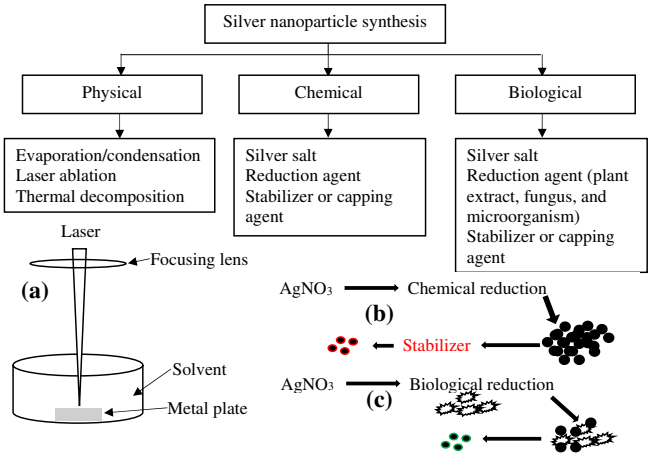


Fig. 3. General procedures to synthesize silver nanoparticles and schematic of the synthesis of silver nanoparticles using (a) physical, (b) chemical, and (c) biological approaches.

medications as well as in the prevention of other diseases is the contributing factor responsible for the growth of AgNPs. This is supported by the fact that AgNPs are effective against gram-positive and gram-negative bacteria as well as antifungal and antimicrobial agents.[7,47–53]

Growing demand for AgNPs in the electronics and electrical fields is predicted to see significant growth until 2022. The increasing demand for products having high performance, high processing capability, more stability, and more conductivity is responsible for the growth of AgNPs in these areas. For textiles, their increase in demand is due to the expanding applications in sportswear, underwear, military clothing, and medical textiles. In addition, their growth in the food and beverages industry is mainly due to increased demand for materials for food storing and processing so that food can stay fresh for longer perids and hygienic. Moreover, the stable rise in demand for other applications of AgNPs is attributed to their utilization in the production of jewelry, coins, photography, and photovoltaics. The aforementioned trend of global AgNP consumption clearly indicates that AgNPs exist widely in the environment. Therefore, environmental effects caused by AgNP release from a wide range of products should be considered. This is critical because these nanoparticles are toxic to fish and the human reproductive system as previously observed.[15–19]

SYNTHESIS OF SILVER NANOPARTICLES

As shown in Figure 3, AgNPs can be synthesized by several approaches including physical, chemical, and biological.[54–56] Figure 3(a)–(c) highlights some main synthetic mechanisms of AgNPs using these approaches. In general, equipment constraints, cost, and time consumption are identified as the major factors influencing the method of synthesis.

Physical approach

Generally, the physical approach used to synthesize AgNPs employs the evaporation–condensation method. It is commonly performed using a tube furnace at atmospheric pressure, which is reliable to synthesize various sizes.[36,57] Several attempts have been made in addition to the above-mentioned studies. A new method was proposed by Tsuji *et al.*[58] for synthesizing AgNPs by a laser ablation technique with focused and unfocused laser beam irradiation carried out at 12 and 900 mJ/cm^2 intensities, respectively. The radiation wavelengths used in their study were 355, 532, and 1064 nm. Their study concluded that the surface plasmon wavelength of AgNPs irradiated using 355, 532, and 1064 nm is ~400 nm for both focused and unfocused schemes.

In a different study, AgNPs were synthesized by using a laser ablation method in solution.[54] In the preparation, silver particles were washed using distilled water and placed in a quartz cell containing 5 mL of high-pressure liquid chromatography (HPLC)-grade water. The study was conducted using the laser operated at 10 Hz repetition rate and 5–9 ns pulse duration. It was found that the average diameter of AgNPs was

12 nm when laser light of 532 nm was applied,whereas the average size of AgNPs prepared using 1064 nm laser light was 31 nm. Their study concluded that the particle size distribution depends on the laser wavelength. The change in particle size was affected by the absorption of laser light by the the particles, which is also well known as fragmentation.[59,60]

To explore the diversity of the technique, AgNPs were synthesized using laser ablation with different laser wavelengths.[61] The diameters of AgNPs were found to be centered around 12, 26, and 29 nm while using 355, 532, and 1064 nm wavelengths, respectively. It was therefore concluded that the silver particle size synthesized using laser ablation can be controlled by varying the laser wavelength. This method was found to be reliable for preparing the desired colloid size in solutions.

In another study, the AgNP sizes obtained from the laser ablation with nanosecond and femtosecond laser pulses were compared.[62] In the preparation, the wavelength of the laser used was 800 nm. In addition, femtosecond laser pulses employed in the study were generated by means of a Ti:sapphire laser system. It was found that the AgNP sizes obtained from the nanosecond laser pulses were smaller than those from femtosecond laser pulses. The mean diameters of AgNPs obtained in the study were 27 and 41 nm for nanosecond and femtosecond laser pulse schemes, respectively.

For technique improvement, synthesizing AgNPs by evaporation/condensation using a small ceramic heater with a local heating area of 500 m^2 was proposed.[63] Pure spherical AgNPs with varying diameters from 6.2 to 21.5 nm were successfully produced. The study concluded that the geometric mean diameter, the geometric standard deviation, and the total number concentration of AgNPs increase with the surface temperature of the heater. Their approach could reliably synthesize stable AgNPs since the temperature of the heater surface did not fluctuate with time.[63]

Employing an alternative approach, AgNPs were synthesized using thermal decomposition by Lee and Kang.[64] Their approach involved an aqueous solution of $AgNO_3$ and sodium oleate. The synthesis was carried out by varying the temperature from room temperature to 290°C with a slow heating rate of 2°C/min for 1 h, when spherical AgNPs with an average size of 9.5 ± 0.7 nm were obtained. To give an overview, other synthesis procedures of AgNPs by means of the physical approach are listed in Table 2.[54,61–83]

Table 2. Synthesis of silver nanoparticles by means of physical approach

Method	Shape	Silver size (nm)	Reference
Laser ablation	Spherical	31	54
Laser ablation	Spherical	12–29	61
Laser ablation	Irregular	27–41	62
Small ceramic heater	Spherical	6–21.5	63
Thermal decomposition	Spherical	9.5 ± 0.7	64
Laser ablation	Spherical	27–120	65
Laser ablation	Spherical	6.48	66
Thermal decomposition	Spherical	14.4 ± 3.3	67
Laser ablation	Spherical	4–18	68
Laser ablation	Spherical	5–13	69
Laser ablation	Spherical	20–51	70
Thermal decomposition	Spherical	4–7	72
Thermal decomposition	Spherical	4.7	73
Laser ablation	Irregular	15–20	74
Laser ablation	Spherical	7.9–16.2	75
Thermal decomposition	Spherical	8.0 ± 1.3	76
Thermal decomposition	Spherical	3.1 ± 0.7 to 4.5 ± 0.8	77
Thermal decomposition	Spherical	40–50	78
Laser ablation	Spherical	2.5–8.5	79
Laser ablation	Spherical	10.6 ± 2.6	80
Laser ablation	Spherical	9–15	81
Laser ablation	Spherical	50	82
Laser ablation	Spherical	5–50	83

Although somewhat good products were achieved using the aforementioned methods, it is worthwhile mentioning that they did exhibit several constraints, such as large space requirement, high energy consumption in raising the surrounding temperature of the source material, as well as taking a long time to achieve thermal stability. As a result, the chemical approach, for instance, has been explored.

Chemical approach

The chemical approach is widely used for synthesizing AgNPs using water or organic solvents. It is an easy way to synthesize AgNPs in solution.[57] However, a certain amount of toxic material may be produced as residue.[56] Some reducing agents such as borohydride, citrate, ascorbate, and glucose have been used to address this problem.[36]

A chemical reduction method was adopted for synthesizing AgNPs of various sizes (7, 29, and 89 nm) using gallic acid.[84] In this work, $AgNO_3$ was used as the silver salt and gallic acid was used as the reducing and stabilizing agent. For 7 and 29 nm AgNPs, the reduction reaction was conducted at pH 11 and 10, respectively. Furthermore, UV light was applied to ionize the phenol groups. In the preparation, for 89 nm AgNPs, it was not necessary to increase the pH value in contrast to the other two sizes. For the 7 and 29 nm nanoparticles, the approach was able to synthesize spherical AgNPs. The 89 nm nanoparticles showed only a pseudo-spherical shape.

A chemical reduction method was proposed for synthesizing AgNPs using $AgNO_3$ as the silver salt, 8% (w/w) sodium dodecyl sulfate as the stabilizing agent, and hydrazine hydrate solution (2.0–12 mM) and sodium citrate solution (1.0 –2.0 mM) as reducing agents.[85] Such a mixture produced AgNPs with a mean diameter of 24 nm for 1.1 Mm $AgNO_3$ solution. Alternatively, $AgNO_3$ was used as silver salt, $NaBH_4$ as the reducing agent, and tri-sodium citrate as stabilizer.[86,87] A 100 mL solution containing $AgNO_3$ and $Na_3C_6H_5O_7$ was prepared by stirring for 30 s. The solution was then added to a 1 mM solution of $NaBH_4$ and was stirred for 60 s. It was found that the diameter of AgNPs decreased slightly with the increase in the amount of borohydride.

$AgNO_3$ as silver salt, aniline as reducing agent, and cetyltrimethylammonium bromide as stabilizer were also used to synthesize AgNPs.[88] Using this method, AgNPs with the sizes of 10–30 nm could be produced. The study concluded that the reducing agent used had no significant effect on the shape, size, or size distribution of AgNPs. Employing a reducing agent and a stabilizer, AgNPs were prepared by adopting $AgNO_3$ as the silver salt, a mixture of hydrazine hydrate and sodium citrate as the reducing agent, and sodium dodecyl sulfate as stabilizer.[47] This method was able to synthesize AgNPs with sizes ranging from 40 to 60 nm.

Nanosilver with different morphologies such as nanocubes, nanowires, and nanospheres could also be produced by polyol synthesis.[89–93] Silver nanocubes were prepared by reducing silver nitrate using ethylene glycol in the presence of poly(vinyl pyrrolidone) and Na_2.[89] It was confirmed that the formation of silver nanocubes was mainly due to the presence of both poly(vinyl pyrrolidone) and Na_2. Using this method, silver nanocubes with controlled edge lengths in the range 18–32 nm could be achieved.[90] For the formation of silver nanowires, nanosilver was affected by the concentration of decahedral multiply twinned nanoparticles that could be obtained by optimizing the molar ratio of poly(vinyl pyrrolidone) and $AgNO_3$ as well as the temperature of the reaction. Another morphology, spherical AgNPs, could be produced by employing ethylene glycol and poly(vinyl pyrrolidone) as the reducing and stabilizing agent, respectively.[91] By altering the heating and injection rates, spherical AgNPs with the sizes of 18 ± 4 and 17 ± 2 nm could be obtained, respectively.

AgNPs were successfully synthesized from a silver ammonia solution (Tollens' reagent, 0.1 mol/L) where particles with sizes from 10 to 30 nm were observed on the surface of bacterial cellulose nanofibers.[94] This approach is an *in situ* event that can be used to synthesize AgNPs through the reaction of Tollens' reagent under ambient conditions. Recently, AgNPs were synthesized from a commercial baby feeding bottle and a food box.[95] This study used a stock silver solution of 1000 mg/L in 2% (v/v) HNO_3, nitric acid (65%), hydrogen peroxide (35%), and milli-Q water. By this approach, it was found that the raw baby bottle plastic produced spherical AgNPs of 500 nm. In the case of the food box, agglomerated AgNPs with an average size of 250 nm were synthesized. This study suggested that this approach could provide accurate information in terms of AgNP size and the number concentration by employing only a short analysis. It is essential to avoid the agglomeration and oxidation of AgNPs so that the analytical inaccuracy can be minimized. For comparison purposes, AgNP sizes obtained from previous studies (including those not discussed in detail here) using different reducing agents and stabilizing or capping agents are summarized in Table 3.[47,55,84–86,88,91–93,96–107]

Biological approach

Recently, the biological approach for synthesizing AgNPs is being increasingly considered. This method is a green technology aimed at minimizing the negative environmental impact. It had been known that the synthesis of AgNPs using the chemical approach requires three main ingredients: a silver salt, a reducing agent, and a stabilizer or capping agent. In the biological approach, the reducing agent and the stabilizer are replaced using molecules obtained from living organisms

Table 3. Synthesis of silver nanoparticles using chemical reduction

Silver salt	Reduction agent	Stabilizer/capping agent	Silver size (nm)	Reference
$AgNO_3$	Hydrazine hydrate and sodium citrate	Sodium dodecyl sulfate	10–20	47
$AgNO_3$	D(+)-Glucose and NaOH	—	8 and 24	55
$AgNO_3$	Gallic acid	Gallic acid	7–89	84
$AgNO_3$	Hydrazine hydrate and citrate of sodium	Sodium dodecyl sulfate	10–20	85
$AgNO_3$	Sodium borohydride	Tri-sodium citrate	~5	86
$AgNO_3$	Aniline	Etyltrimethlyammonium bromide	10–30	88
$AgNO_3$	Ethylene glycol	Poly(vinyl pyrrolidone)	50–175	92
$AgNO_3$	Ethylene glycol	Poly(vinyl pyrrolidone)	8–10	93
$AgNO_3$	NaOH	Polyanionic Na + poly(γ-glutamic acid)	17.2 ± 3.4 to 37.3 ± 5.5	96
$AgNO_3$	Trisodium citrate dehydrate (TSC) and potassium tartrate	Poly(vinyl pyrrolidone), sodium dodecyl sulfate (SDS)	20–100	97
$AgNO_3$	Glucose	Poly(vinyl pyrrolidone)	20–80	98
$AgNO_3$	Poly(vinyl pyrrolidone) and gelatin	Glucose, fructose, lactose, and sucrose	35	99
$AgNO_3$	D-Glucose	carboxy methyl cellulose, NaOH	5–15	100
$AgNO_3$	Poly(ethylene glycol)	Poly(ethylene glycol)	15–30	101
$AgNO_3$	Poly(ethylene glycol)	—	10–80	102
$AgNO_3$	NaOH and Sodium borohydride	Oleic acid (OA) and poly(acrylic acid) (PAA)	13–478	103
$AgNO_3$	Ethylene glycol	Poly(vinyl pyrrolidone)	17 ± 2	91
$AgNO_3$	Ethylene glycol	—	17–70	104
$AgNO_3$	Alkali lignin (low sulfonate)	Alkali lignin (low sulfonate)	7.3 (±2.2) and 14.3 (±1.8)	105
$AgNO_3$	NaOH	Alkali lignin (low sulfonate)	5–100	106
$AgNO_3$	Sodium borohydride	—	3.5–6	107

such as plants, bacteria, fungi, yeast, and algae; their details are discussed in the following sections.

Plant extracts

Plant extracts can work as reducing agents to synthesize AgNPs and provide an alternative solution that is environmentally friendly. As a naturally occurring resource, it is additionally less costly and abundantly available in the environment. Figure 4 shows several plant extracts used to synthesize AgNPs from their leaves, seeds, roots, and fruits.[108–127] In the following, several plant extracts used in various studies to produce AgNPs and are of interest are described.

A biological approach was proposed using the leaf extracts of five plants (pine, persimmon, ginkgo, magnolia, and platanus) as reducing agents.[56] It was noticed that the reaction temperature, leaf broth concentration, and $AgNO_3$ could be used to control the AgNP size. The study concluded that the magnolia leaf broth was the best reducing agent in synthesizing AgNPs in terms of synthesis rate and conversion. The approach was able to synthesize AgNPs of 15–500 nm sizes on average.

A procedure to synthesize AgNPs was presented using the seed extract of *Jatropha curcas*.[122] In the preparation, six different concentrations of $AgNO_3$ from 10^{-3} to 10^{-2} M were applied. The solutions were heated at a temperature of 80°C and were characteristically reddish after heating for 15 min. It was found that AgNPs at different concentrations were mostly spherical in shape and in the diameter range 15–50 nm. The study concluded that the AgNP size could be controlled by varying the $AgNO_3$ concentration. Alternatively, a biological approach was employed for synthesizing AgNPs using *Acalypha indica* leaf extract.[128] In the synthesis, 100 mL of $AgNO_3$ and 12 mL of the aqueous extract of *A. indica* were mixed in an Erlenmeyer flask. The synthesis was conducted under static conditions at a temperature of 37°C. The study noted that the process should be carried out in the dark to minimize the

Fig. 4. Synthesis of silver nanoparticles using plant extracts: (a) *Abutilon indicum*[123], (b) *Skimmia laureola*[126], (c) *Lantana camara*[125], (d) *Prunus yedoensis*[109], (e) *Adenium obesum*[117], (f) *Coffea arabica*[119], (g) *Bunium persicum*[112], (h) *Vigna radiata*[120], (i) *Artocarpus heterophyllus* Lam[108], (j) *Jatropha curcas*[122], (k) *Ocimum sanctum*[127], (l) *Morinda citrifolia*[111], (m) beetroot[121], (n) *Justicia Adhatoda*[114], (o) *Zingiber officinale*[110], (p) *Vitis vinifera*[115], (q) *Crataegus douglasii*[116], (r) *Emblica Officinalis*[124], (s) *Terminalia chebula*[118], and (t) *Piper longum.*[113]

photoactivation of $AgNO_3$. It also concluded that spherical AgNPs of 20–30 nm average size can be synthesized using this method.

The effect of extracts from the callus and leaf of *Sesuvium portulacastrum* L. was examined in the synthesis of AgNPs.[129] For the extraction of the callus or leaf, the source material was first ground, boiled for 5 min, and then centrifuged at 3000 rpm. Furthermore, the extract was mixed with 45 mL aqueous 10^{-3} M $AgNO_3$. It was reported that spherical AgNPs of size ranging from 5 to 20 nm could be obtained using this method. The study concluded that for AgNP synthesis, the callus extract was superior to the leaf extract in terms of stability and color intensity of the nanoparticles.

Alternatively, a biosynthetic approach was adopted using *Mentha piperita* as a bioreducing agent for silver nitrate and chloroauric acid (HAuCl4).[130] In the preparation, 1.5 mL of plant extract was added to 30 mL of $AgNO_3$ per 1 mM/mL solution. The reaction was conducted at a temperature of 28°C for 24 h. The solution was then centrifuged at 6000 rpm for 10 min. Spherical AgNPs with the average size of about 90 nm and gold nanoparticles of 150 nm could be synthesized by this method.

Table 4. Synthesis of silver nanoparticles by means of biological reduction using plants extract

Silver salt	Plant origin	Shape	Silver size (nm)	Reference
$AgNO_3$	Pine, persimmon, ginkgo, magnolia, and platanus	—	15–500	56
$AgNO_3$	*Artocarpus heterophyllus Lam*	Irregular	10.78	108
$AgNO_3$	*Prunus yedoensis*	Spherical and oval	20–70	109
$AgNO_3$	*Zingiber officinale*	—	10–20	110
$AgNO_3$	*Morinda citrifolia*	Spherical	30–55	111
$AgNO_3$	*Bunium persicum*	Spherical	20–50	112
$AgNO_3$	*Justicia Adhatoda*	Spherical	~25	114
$AgNO_3$	*Adenium obesum*	Spherical	10–30	117
$AgNO_3$	*Coffee arabica*	Spherical and ellipsoidal	20–30	119
$AgNO_3$	*Vigna radiata*	Spherical and oval	5–30	120
$AgNO_3$	*Jatropha curcas*	Spherical	10–20	122
$AgNO_3$	*Emblica Officinalis*	—	10–20	124
$AgNO_3$	*Lantana camara*	Spherical	14–27	125
$AgNO_3$	*Sesuvium portulacastrum* L.	Spherical	5–20	129
$AgNO_3$	*Mentha piperita*	Spherical	90	130
$AgNO_3$	*Tribulus terrestris* L.	Spherical	16–28	131
$AgNO_3$	*Musa balbisiana*, *Azadirachta indica*, and *Ocimum tenuiflorum*	Spherical, triangular, and cuboidal	100	133
$AgNO_3$	*Nyctanthes arbor-tristis*	Spherical	50–80	134
$AgNO_3$	*Sesuvium portulacastrum* L.	Spherical	5–20	129
$AgNO_3$	*Azadirachta indica*	Spherical	50–100	140
$AgNO_3$	*Pelargonium graveolens*	Spherical	16–40	141
$AgNO_3$	*Vigna sp. L*	Spherical	24.35	142
$AgNO_3$	*Cinnamomum camphora*	Spherical	55–80	143
$AgNO_3$	*Bauhinia variegata*	Spheres, triangle, truncated triangles, and decahedrons	38–65	144
$AgNO_3$	*Aloe vera*	Spherical	15.2 ± 4.2	145
$AgNO_3$	*Amaranthus retroflexus*	Spherical	10 to 32	146

AgNPs can also be synthesized using plant fruit bodies. For instance, *Tribulus terrestris* L. fruit bodies were employed as the reducing agent.[131] The proposed method could be used to synthesize spherical AgNPs with sizes ranging from 16 to 28 nm. The study claimed that the natural reducing agent offers a quick solution to convert the silver ions (Ag^+) to metallic AgNPs (Ag0). The use of $AgNO_3$ as the silver salt and ethanol as stabilizer to synthesize AgNPs using the plant *R. hymenosepalus*, which acted as the reducing agent, was also examined.[132] It was found that the diameters of the AgNPs obtained were in the range 2–40 nm.

Leaf extracts of three plants, *Musa balbisiana* (banana), *Azadirachta indica* (neem), and *Ocimum tenuiflorum* (black tulsi), were used as biological reduction agents to produce AgNPs.[133] In the preparation, silver nitrate (1 mM) was mixed with 5% leaf extract of each type of plant separately in 250 mL Erlenmeyer flasks. The different leaf extracts used in the synthesis yielded different shapes of AgNPs, such as spherical, triangular, and cuboidal for banana, neem, and tulsi extracts, respectively. The resulting AgNPs sizes were below 100 nm. In another study, the use of the extract from the seeds of *Nyctanthes arbor-tristis* as the reducing and capping agent to synthesize AgNPs was explored.[134] The study was carried out at room temperature. The mixture was centrifuged at 3000 rpm for 15 min. It was reported that uniform spherical AgNPs within 50–80 nm could be obtained using the method.

AgNPs can be alternatively synthesized using tea or coffee extract.[119,135–138] The use of these extracts has been proven to be eco-friendly. Commercialized brands

such as Folgers, Sanka, and Starbucks coffee and Bigelow, Luzianne, and Lipton tea had been used to synthesize silver and palladium nanoparticles in aqueous solutions.[135] Spherical nanoparticles with the size ranging from 20 to 60 nm were successfully produced when the above-mentioned coffee or tea extracts were employed. In addition, black tea extracts have the capability to reduce $AgNO_3$ to spherical AgNPs and other morphologies such as nanoprisms and nanorods in the size range of 20 nm.[136] Recently, green and Arabica coffee beans were found to have the ability to perform as reducing and stabilizing agents to produce AgNPs.[119,138] Spherical and ellipsoidal nanoparticles with the size ranging from 20 to 30 nm could be produced by employing Arabica coffee, while almost spherical AgNPs in the range of 10 to 30 nm were successfully extracted by the green coffee beans.

Recently, a biological route for the synthesis of nanoparticles was proposed using different concentrations of silver nitrate from 20 to 0.62 mM mixed with an aqueous plant extract ranging from 100 to 0.79 mg/mL.[139] In the method, 100–1000 mg of the dried leaves of *Artemisia absinthium* in powder form was boiled in 10 mL deionized water for 5 min. Irregular shapes of silver particles in the size range 5–20 nm were obtained. The study concluded that larger silver particles could be obtained from a higher concentration of the plant extract or silver nitrate. A summary of the plants used in the synthesis of AgNPs in numerous studies is listed in Table 4.[56,108–112,114,117,119,120,122,124,125,129–131,133,134,140–146]

Fungus as reduction agents

In addition to plant extracts, fungi also can be used to synthesize AgNPs. A procedure was suggested to synthesize AgNPs from silver nitrate using the fungus *Verticillium*.[147] From the study, it was found that the average AgNP size was 25 ± 12 nm. *Fusarium oxysporum* was also tried as a biological reducing agent to synthesize AgNPs.[148] Silver nitrate of 10^{-3} M was mixed with 10 g of *Fusarium oxysporum* biomass in a conical flask containing 100 mL of distilled water. Using the proposed method, spherical and occasionally triangular AgNPs in the size range 5–15 nm were fabricated.

Employing the fungus *Aspergillus flavus*, AgNPs were synthesized from silver nitrate.[149] In the preparation, 1 mM silver nitrate was mixed with 5 g of the fungus. The solution was incubated in a shaker at 200 rpm at a temperature of 37°C in the dark. Furthermore, the pH of the solution was adjusted to 6.2 ± 0.2. The study found that the average AgNP size was 8.92 nm. Alternatively, the fungus *Cryphonectria* sp. was used as reducing agent of silver nitrate.[150] Silver nitrate was mixed with 15 g of fungal biomass in a conical flask containing 100 mL of distilled water. The study was conducted at a temperature of 25°C in the dark. The AgNP sizes were found to be in the range 30–70 nm. Also, the concentration of AgNPs was 6.82 × 108 particles per milliliter of solution.

Using a different fungus, *Humicola* sp., synthesis of AgNPs was proposed.[151] In the preparation, Erlenmeyer flasks of 250 mL containing 100 mL of malt extract (0.3%), glucose (1%), yeast extract (0.3%), and peptone (0.5%) medium were used to grow the fungus *Humicola* sp. The pH of the solution was adjusted to 9 using sterile 10% sodium carbonate. The study reported that spherical AgNP sizes of 5–25 nm could be produced.

The biggest advantage of biological synthesis based on fungal enzymes is the possibility of developing a rational approach for the biosynthesis of nanomaterials over a range of chemical compositions, which is currently not possible by other microbe-based methods.[148] In addition, the biological approach provides an alternative method that is environmentally friendly since they are free of chemical toxins.[152] AgNPs synthesized by various fungi are shown in Table 5.[147–151,153–163]

Microorganisms as reduction agents

Microorganisms such as bacteria and yeast are recently considered as alternative reduction agents to rapidly synthesize AgNPs. A rapid method of synthesis of AgNPs using the culture supernatants of *Klebsiella pneumonia*, *Escherichia coli*, and *Enterobacter cloacae* was proposed.[164] It was shown that AgNPs can be synthesized within 5 min, with particle sizes from 28 to 122 nm with the average size of 52.5 nm. Recently, synthesis of AgNPs was carried out by employing a probiotic strain *B. licheniformis* Dahb1 as the reducing agent of silver nitrate.[152] The probiotic was incubated in a flask containing a sterile nutrient broth at a temperature of 37°C for 24 h. Spherical AgNP sizes in the range 18–63 nm were obtained. Table 6 summarizes the various microorganisms used to synthesize AgNPs.[152,164–174]

Table 5. Synthesis of silver nanoparticles by means of biological reduction using fungus

Silver salt	Fungus	Shape	Silver size (nm)	Reference
$AgNO_3$	*Verticillium*	—	25 ± 12	147
$AgNO_3$	*Fusarium oxysporum*	Spherical	5–15	148
$AgNO_3$	*Aspergillus flavus*	—	8.92	149
$AgNO_3$	*Cryphonectria* sp.	—	30–70	150
$AgNO_3$	*Humicola* sp.	Spherical	5–25	151
$AgNO_3$	*Phaenerochaete chrysosporium*	Pyramidal	50–200	153
$AgNO_3$	*Cochliobolus lunatus*	Spherical	3–21	154
$AgNO_3$	*Penicillium chrysogenum* and *Aspergillus oryzae*	Spherical	6–100 and 14–76	155
$AgNO_3$	*Amylomyces rouxii*	Spherical	5–27	156
$AgNO_3$	*Aspergillus flavusNJP08*	Spherical	17 ± 5.9	157
$AgNO_3$	*Aspergillus niger*	Spherical	3–30	158
$AgNO_3$	*Alternaria alternata*	Spherical	20–60	159
$AgNO_3$	*Aspergillus tamarii* PFL2, *A. niger* PFR6, and *Penicllium ochrochloron* PFR8	Spherical	3.5 ± 3, 8.7 ± 6, and 7.7 ± 4.3	160
$AgNO_3$	*Aspergillus fumigatus*	Spherical	5–25	161
$AgNO_3$	*Rhizopus stolonifer*	Spherical	9.47	162
$AgNO_3$	*Cladosporium sphaerospermum*	Spherical	15.1 ± 1.0	163

PROPERTIES OF SILVER NANOPARTICLES

In order to maximize the potential applications of AgNPs, a proper knowledge of their properties is crucial. The advantages and disadvantages of using AgNPs must be clearly quantified and qualified to know their effects on the environment. Intensive efforts have been made to investigate and explore the benefits of AgNPs in several applications.[2,15] Also, many researchers have investigated the adverse effects of AgNPs.[175] In this section, the properties of AgNPs such as their morphologies and sizes, crystalline structures, toxicity, as well as their optical, electrical, and catalytic properties are examined.

Morphologies and sizes

Morphologies and sizes of AgNPs depend greatly on the concentration of the solution.[176] For instance, their distribution and size vary with the concentration of both the polysaccharides and the precursor metal salts.[176] The study found that larger particles and Ag clusters were obtained by increasing the $AgNO_3$

Table 6. Synthesis of silver nanoparticles by means of biological reduction using microorganisms

Silver salt	Microorganisms	Shape	Silver size (nm)	Reference
$AgNO_3$	*Bacillus licheniformis*	Spherical	18–63	152
$AgNO_3$	*Klebsiella pneumonia*, *Escherichia coli*, and *Enterobacter cloacae*	—	28–122	164
$AgNO_3$	*Pseudomonas antarctica, P. proteolytica, P. meridiana, Arthrobacter kerguelensis, A. gangotriensis, Bacillus indicus, and B. cecembensis*	Spherical	6–13	165
$AgNO_3$	*Bacillus subtilis*	Spherical	5–60	166
$AgNO_3$	*Staphylococcus aureus*	—	160–180	167
$AgNO_3$	*Klebsiella pneumonia*	Spherical	1–6	168
$AgNO_3$	*Nocardiopsis* sp. MBRC-1	Spherical	45 ± 0.15	169
$AgNO_3$	*Serratia nematodiphila*	Spherical	10–31	170
$AgNO_3$	*Bacillus subtilis* and *Klebsiella pneumonia*	Spherical	20–50	171
$AgNO_3$	*Deinococcus radiodurans*	Spherical	4–50	172
$AgNO_3$	*Bacillus pumilus, B. persicus,* and *B. licheniformis*	Spherical	77–92	173
$AgNO_3$	*Gluconacetobacter xylinus*	Spherical	40–100	174

concentration from 2.5 to 15 mM. Larger spherical Ag nanoparticles were obtained with an increased concentration of the polysaccharide.

AgNPs in several sizes and morphologies using numerous reducing and capping agents were obtained by Shervani *et al.*[55] Their study reported that 1 wt% reduction of an aqueous starch solution of $AgNO_3$ using D(+)-glucose and NaOH at a temperature of 70°C for 30 min can produce spherical AgNPs of 15 and 43 nm in diameter. Their study also analyzed the effects of the reducing agent on AgNP sizes at ambient temperature. It was found that spherical silver particles of 8 and 24 nm diameter were obtained when applying the reducing agent on the silver salt in liquid crystalline pluronic P123 and L64. In another treatment, when the $AgNO_3$ precursor salt was reduced by NaOH in an ethylene glycol (11 g)/polyvinyl pyrrolidone (PVP; 0.053 g) mixture, AgNPs were obtained in large self-assembled cubes of 520 nm. The authors concluded that the capping agents PVP and poly(methyl vinyl ether) (PVE) act as shape-modifying agents in synthesizing AgNPs into several shapes such as pure cubes, stars, and mixed geometry. On the contrary, applying the reducing agents using D(+)-glucose and NaOH in a water-soluble form could produce spherical AgNPs.

It is well established that the properties of AgNPs are greatly dependent on their morphology. The morphological change is a consequence of complex combinations of molecular, surface, and crystalline characters.[177] To maximize their properties, several shape- and size-controlled synthesis procedures of AgNPs have been proposed and revised.[178–181] The relationships between their morphology such as shape and size to certain properties are now well understood. For instance, their antibacterial activity is more effective as a result of the large surface-to-volume ratio of isotropic geometry such as that of spherical shape compared to the anisotropic geometry.[182] Since AgNPs can interact with a bacterial cell, smaller particles having a larger surface area are the most effective as antibacterials compared to those of larger size.[183] For plasmonic properties, the larger particles have a wider UV–vis absorption spectra than smaller particles.[183] Moreover, their thermodynamic properties are also affected by their nanoparticle sizes. For instance, bulk silver has a molar heat capacity that is lower than that of AgNPs due to their surface free energy.[184] In addition, it has been shown that the molar entropy of nanoparticles is higher than that of bulk silver. This is due to the entropy associated with the first derivatives of Gibbs free energy.

A review study reported that the common sizes of AgNPs used in general applications range from 1 to 10 nm.[185] AgNP size can affect its surface area-to-volume ratio and their quantum confinement. AgNP size can also affect the existence of virus or bacteria.[186] For instance, an *in vitro* study has shown that AgNPs in the range 1–10 nm can interact with the HIV-1 virus through binding to the host cells.[187] Moreover, the truncated triangular nanoparticles demonstrated the strongest biocidal action against the gram-negative bacterium *Escherichia coli* compared to the spherical and rod-shaped nanoparticles.[188]

Toxicity properties

The unique chemical properties of AgNPs can be well exploited in several applications. Studies have proven that AgNPs are very effective as antimicrobials against bacteria, viruses, and eukaryotic microorganisms.[15,187,189] Since silver AgNPs are known to exist in several commercial products such as contraceptive devices and feminine hygiene products, they may have adverse effects on the human reproductive system.

Antimicrobial activity of AgNPs against *E. coli* was evaluated by Martínez-Castañón *et al.*[84] The study used different concentrations of AgNPs from 10 to 100 μg/cm^3. It was found that the concentration of 10% AgNPs inhibited bacterial growth by 70%. Interestingly, when the concentration was increased from 50 to 60 μg/cm^3, bacterial growth was inhibited by 100%. Another finding of the study was that the inhibition of bacterial growth also depended on the number of cells used in the study.

In the use of consumer products, human skin exposure to toxic AgNPs may increase since these materials are intensively employed in several cosmetics and textiles. AgNPs can be released from consumer products depending on the quantity of silver coating, the fabric quality, pH, and sweat formation.[190] Using an artificial human skin, AgNPs were found to be released from antibacterial fabric products into the sweat.[191] In another study, based on an *in vitro* approach, AgNPs induced cell death and oxidative stress in human fibrosarcoma and skin carcinoma cells. In addition, intensive

works have proved that AgNPs can decrease cell proliferation and chemotaxis of the human mesenchymal stem cells, increase cytotoxicity and oxidative stress of the human hepatoma HepG2 cells, and can have several other adverse effects.[192–197] The above-mentioned toxicity of AgNPs strongly depends on their sizes and doses.

Although their toxicity mechanisms are still under debate, several possible routes have been suggested. For instance, the interaction between AgNPs and constituents of the bacterial membrane caused structural changes and eventual damage followed by the bacterial cell death.[15] Alternatively, AgNPs inhibit the respiratory enzyme of bacteria and facilitate the generation of reactive oxygen, leading to cell damage.[188,198] Moreover, it is also possible that the toxicity mechanisms are due to the chemical transformation during intracellular processes of the nanoparticles. To understand this transformation, a potential procedure by integrating synchrotron radiation transmission X-ray microscopy (SR-TXM) and SR-X-ray absorption near edge structure (SR-XANES) spectroscopy was recently proposed.[199] Using this approach, the 3D distribution of AgNPs inside a single human monocyte was successfully captured with their chemical transformation. The relevant study also confirmed that the transformations of particulate silver from the elemental silver (Ag^0) to Ag^+ ions, Ag-0, and then to Ag-S- species are the main mechanisms characterizing their toxicity.

Crystalline structures

Crystalline structure of AgNPs can be derived from X-ray diffraction patterns. Several studies reported that AgNPs have the cubic structure,[149,176] showing peaks at 38.06°, 44.22°, 64.48°, and 77.32° corresponding to the scattering angle 2θ from the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes, respectively.[176] In addition, the diffraction pattern of AgNPs occurs at 38.5°, 44° and 64.5° (2θ).[149] These patterns can be indexed to the (111), (200), and (220) planes of the face-centered cubic (fcc) silver.

Optical properties

Several studies have shown that AgNPs absorb electromagnetic radiation in the visible region from 380 to 450 nm by means of a phenomenon known as the excitation of localized surface plasmon resonance (LSPR).[200,201] The spherical shape of AgNPs synthesized by glucose reduction was found to have surface plasmon resonance at 400 nm.[55] In addition, for the same shape of AgNPs obtained from NaOH reduction, their study found that the nanoparticles absorbed the maximum electromagnetic radiation at 420 nm.

Alternatively, AgNPs synthesized in different sizes using gallic acid using an aqueous chemical reduction method were characterized by Martínez-Castañón *et al.*[84] Their study demonstrated that spherical AgNPs with the size of 7 nm have a surface plasmon resonance at 410 nm while those with 29 nm size have a resonance at 425 nm. In addition, AgNPs of size 89 nm exhibited a wider band with a maximum at 490 nm. It was noticed that the width of surface plasmon resonance was related to the nanoparticle size distributions.

Irregularly shaped AgNPs can have two or more plasmon resonances depending on the nanoparticle symmetry.[188] The above findings show that AgNPs have the potential to be exploited in sensor devices. Recently, their unique properties have been capitalized for their use as sensors for sensitive colorimetric detection of chromium in surface waters, industrial wastewater, and vegetable samples.[202] In addition, their superior properties were used for the determination of the critical micelle concentration of cationic surfactants.[203] Also, their antimicrobial capability was found to depend on the surface plasmon resonances.[204] Moreover, an AgNP-based sensor provides a pathway to ultrasensitive biodetection experiments with extremely simple, small, light, robust, and low-cost instrumentation.[205] It had been demonstrated that the presence of AgNPs in surface-enhanced Raman scattering (SERS) filter paper improves their signal intensity.[206] Alternatively, they can be used for improving the performance of solar cells.[207]

Thermal properties

Thermal behavior is an important aspect that is considered in detail in the production or application of a material. A remarkable property of metal nanoparticles is their low melting temperature due to the thermodynamic size effect. It was widely applied for several purposes. Thermogravimetric analysis (TGA) or differential scanning calorimeter (DSC) is commonly employed to examine the thermal properties of AgNPs. Another technique to theoretically study the thermal

property of nanoparticles is by using the Gibbs–Thomson equation.

Specifically, the melting temperature of a material is critical for several applications. In bulk material, the surface-to-volume ratio is small so that surface effects on the melting point can be ignored. Conversely, for nanomaterials that have a large surface-to-volume ratio, the melting point is size-dependent. This phenomenon can be well explained using thermodynamic theory. To prove this theory, several experiments have been conducted.[208,209] These studies investigated the melting points of AgNPs having sizes ranging from 4 to 50 nm. It was found that when the size of AgNPs decreased, melting occurred at lower temperatures.

In a different study, the thermal behavior of AgNPs having sizes of 3 to 6 nm was examined.[210] It was found that AgNPs heated at a temperature of 100°C showed no significant change in terms of size. On the other hand, those heated at a temperature of 150°C showed a dramatic increase in their melting point. In addition, the particle size of AgNPs progressively increased at 200°C, indicating complete melting. Moreover, this melting point was also confirmed by DSC curves showing a sharp exothermic peak around 150°C.

Bulk silver generally has a thermal conductivity of 429 W/m/K. A study by Son *et al*. found that AgNPs have a thermal conductivity of 0.37 W/m/K.[210] The lower value obtained from the study indicated the presence of organic surfactants coated on the nanoparticles and therefore serving as their stabilizer in the solution.

Electrical properties

AgNPs with their unique electrical properties can be utilized in electronic devices. The electrical conductance of AgNPs varying in size from 4 to 12 nm that were grown in glass-ceramic was examined.[211] The DC electrical resistance of AgNP films was measured in the temperature range 80–300 K. It was found that the surface resistivity increases linearly with temperatures rising from 120 to 300 K. Another important finding from the study was that the effective Debye temperature increased with the rise in the AgNP size.

Alternatively, AgNPs were employed as conductive fillers in electronically conductive adhesives (ECAs).[10] The study found that the presence of AgNPs in ECAs decreased the resistivity, indicating that it is more conductive compared to the medium without AgNPs. The above findings prove that AgNPs have the potential to be exploited in electrical devices.

The zeta potential (which is usually denoted using the Greek letter ζ) is a scientific term defining the electrical potential in colloidal dispersions. This parameter represents the charge of a particle in the suspension. In addition, it can be used as an indicator of the potential stability of the colloidal system. Dynamic light scattering (DLS) is the widely used method for characterizing this parameter.[212–214] A large negative or positive zeta potential of all the particles in suspension indicates that they tend to repel each other and there is no tendency to flocculate. Conversely, a low negative or positive value of this value shows that the particles tend to flocculate.

Because of this relationship, the zeta potential of the spherical and hexagonal AgNPs was examined by Singh *et al*.[213] They found that spherical and hexagonal AgNPs had a potential of −5.11 and −15.3 mV, respectively. These findings indicate that hexagonal AgNPs are more stable than spherical ones. Anisotropic nanoparticles have more edges compared to isotropic, and their surface area is also higher. As a result, more negative charge can be seen on the anisotropic nanoparticles.

Catalytic properties

AgNPs have been utilized as effective catalytic agents for the reduction of various dyes such as methylene blue, yellow-12, 4-nitrophenol, Rose Bengal, eosin, and methyl orange.[215–219] AgNPs synthesized using the peach kernel shell method were found to have the capability as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol.[215] The reduction process could take 200 min without the catalyst. In contrast, in the presence of the catalyst, the reduction was completed in 105 s with the optimum parameters of 250 mM $NaBH_4$ and 10.0 mg AgNPs. As comparison, the reduction of 4-nitrophenol can also be achieved by employing gum acacia-Pt nanoparticles, resin-Au nanoparticles, Ni-polyvinylamine/SBA-15 composite, AgNP-seashell, and silver/TiO_2 nanocomposite with complete reduction taking 8 h, 20 min, 85 min, 4.5 m, and 2 min, respectively.[220–224] In terms of time, AgNPs-peach kernel shell is the best among the aforementioned proposed catalysts. In addition, their nanoparticles have been found to reduce methyl orange faster than Cu

nanoparticle-mesoporous silica SBA-15, AgNP-seashell, and silver/TiO_2 nanocomposite.[223–225] Similar finding was found when the nanoparticles were applied to reduce methylene blue more efficiently compared to AgNP-seashell, porous Cu microspheres, and silver/TiO_2 nanocomposite.[223,224,226]

The reduction mechanisms of several dyes using AgNPs in the presence of $NaBH_4$ are well established and proven to follow the Langmuir–Hinshelwood model.[217,218,227] $NaBH_4$ acts as an electron and hydrogen donor changing the entire solution pH.[217,218] The process is followed by the change of the surface charge of the AgNP to positive before BH_4^- and the dye is concomitantly adsorbed on the surface of AgNPs. The AgNPs then receive electrons from BH_4^- and convey them to the dye molecules.[228] Also, a large volume of hydrogen supplied by $NaBH_4$ in the presence of AgNPs renders the hydrogenation of azo dyes. In addition, the large surface area of AgNPs can cause the desorption of the final product to colorless.[218]

FUTURE CHALLENGES

Synthesis procedure

Although green synthesis of AgNPs is favorable compared to chemical and physical procedures, this synthesis process should also consider its simplicity, cost, and time consumption. Synthesis procedures using mediated fungus, bacteria, and other organisms are difficult since they involve the isolation and growth of the strains, which are intricate operations requiring several complicated steps. Also, these procedures are problematic in terms of maintaining the culture medium as well as the physical and chemical conditions. Plant extracts are recently considered because of their ease of extraction, abundant availability, and their potential to eliminate the above-mentioned complicated procedures of cell culture maintenance.

Synthesis methods of AgNPs using leaves, seeds, roots, and fruits are well established. Accessibility of seeds and roots is slightly difficult compared to leaves and fruits. While fruits are considered vitamin sources for human health, they are, however, uncommon for nanomaterial production. Furthermore, leaves are abundantly available and commonly discarded to the environment.

For AgNP production, biological synthesis using leaf extracts has been demonstrated to be more suitable for producing the spherical shape, as can be seen in Table 4. As previously mentioned, the properties of AgNPs are crucially dependent on their morphology and size. For synthesizing AgNPs in other shapes, syntheses using *Musa balbisiana*, *Azadirachta indica*, *Ocimum tenuiflorum*, *Bauhinia variegate*, or *Prunus yedoensis* have been considered as alternatives for further exploration.[109,133,144] In general, future challenges in green synthesis procedure lies in how this procedure can be used to uniformly produce other forms such as triangular, cuboidal, truncated, decahedral, oval, ellipsoidal, and pyramidal shapes.

Release to the environment

Since AgNPs are released into the environment from various commercial products and have toxicity that can potentially damage the environment, a proper knowledge of their transport behavior is crucially needed. It is essential to clearly quantify and qualify the existence of silver in the environment. Several reports have shown that the transportation of AgNPs depends on the environmental conditions and the particles'properties.[229–231]. In the environment, Ag(0) can be transformed into different forms, such as ionic Ag, Ag_2O, and Ag_2S.[229] Several recent studies have focused only on the calculation of the AgNP release concentration,[20–22,232–234] whereas very little investigation on the impact due to their release has beeen done. Also, their transportation mechanism after release into the environment is still an unsolved matter.

Several proposed mathematical models for the transportation AgNPs in soil such as colloid filtration and convection–dispersion theories are reliable for small-scale consideration by soil column study using disturbed or undisturbed soil, although sometimes the soil is assumed to be uniform.[235–241] This condition is contrary to the fact that soil is a relatively complex medium and the way AgNPs can transform, as previously discussed. Also, there exist little information on AgNP behavior in water systems.

It had been found that the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory commonly used for the AgNP aggregation has limitations.[242] It was noticed that this theory was unsuccessful in predicting the aggregation kinetics of sterically and electrostesrically stabilized AgNPs. Since several capping agents are included in their synthesis, this theory poorly predicted their aggregation.[185] Moreover, in this classical theory, the particle shape is generally assumed to be spherical,

which is not true; practical shapes can also be triangles, icosahedrons, ellipses, rhombohedrons, spindle, rod, or tubes.[243] Furthermore, the behavior of AgNPs in the air after their release has not been evaluated and investigated. The aforementioned issues are worthy of further studies.

Scaled-up silver nanoparticle synthesis

One major issue in early nano production research was concerned with how they can be produced on a large scale. Scaling up of nanomaterial production from laboratory processes to industrial scale is difficult and has many uncertainties. There are two challenges for scaling up nanomaterial production, which are based on their production and properties, that should be carefully considered. First, their production should consider the cost, reliability, wastage, energy consumption, possibility of recycling, material safety, and hazard level. Second, nanomaterials' properties possibly change when scaled up; particularly, the level of control applied at the nanoscale has a tendency to decrease when dealing with large quantities.

There are many reports on the potential of AgNP production on a large scale using batch reactors.[244–249] In general, these investigations focus on the optimum parameters in the synthesis processes such as concentration, time, reducing agent, and stabilizer or combination effects with physical treatment such as heating, stirring, or sintering.

Among these, a study combining chemical and physical approaches for producing AgNPs on a large scale was completely documented starting from the evaluation to AgNP production.[249] Silver nitrate, formaldehyde, and trisodium citrate were used as the silver salt, reductant, and stabilizer, respectively, with microwave (MW) dielectric heating as the heating source. The study reported that AgNPs can be rapidly synthesized on a large scale (up to 100 mmol/L). Another study also claimed to be able to synthesize about 20 ± 1.3 mg AgNPs from 30 mg silver nitrate dissolved in ethylene glycol and poly(*N*-vinyl pyrrolidone) using a microwave-assisted process.[248]

The aforementioned procedures are significant for initiating the investigation of the large-scale synthesis of AgNPs. A common weakness with these procedures, however, is that AgNPs cannot be continuously produced. For industrial scale-up, the production should be continuous because it is critically related to the operational cost. A prototype using a continuous flow tubular microreactor has been considered as an alternative.[250] In the flow reactor, AgNPs can be produced on a continuous basis once the reaction reaches the steady state. In addition, it needs only timescales of seconds or even milliseconds to achieve the targeted reaction temperatures. Moreover, the benefit of this method is it can be easily scaled up by increasing the reactor length. Furthermore, this procedure has the potential to synthesize AgNPs using green approaches.

Case study on the utilization of silver nanoparticles in Malaysia

Malaysia, as a developing country, recently has paid attention to the development of nanotechnology. For this purpose, the Malaysian government has established a special directorate called the National Nanotechnology Directorate (NND) under the Malaysian Ministry of Science, Technology and Innovation (MOSTI). The directorate was established on January 13, 2010, and officially began operations in July 2010. Several institutions were also established to support the development, such as the Ibnu Sina Institute for Fundamental Science Studies (IIS), Universiti Teknologi Malaysia; Institute of Microengineering and Nanotechnology (IMEN), Universiti Kebangsaan Malaysia; Centre of Innovative Nanostructures and Nanodevices (COINN), Universiti Teknologi PETRONAS (UTP); Institute of Nanoelectronics Engineering, Universiti Malaysia Perlis (UniMAP); Nanoscience and Nanotechnology Research Group, International Islamic University Malaysia (IIUM); Institute of Advanced Materials (ITMA), Universiti Putra Malaysia (UPM); NanoOpto-Electronics Research Lab (NOR LAB), Universiti Sains Malaysia (USM); Nanotechnology and Catalysis Research Centre (NANOCAT), Universiti Malaya (UM); and the NEMS/MEMS Research Laboratory, MIMOS. Furthermore, companies involved in nanotechnology production such as Nanopac, Nano-Malaysia Berhad, and Nano Silver Manufacturing Sdn Bhd (NSM) were rapidly established in Malaysia.

In recent years, there has been increased interest on the study of AgNPs in Malaysia due to their superior properties, as previously discussed. Studies on AgNPs in Malaysia as identified in Scopus started in 2004. To date, the total number of publication related

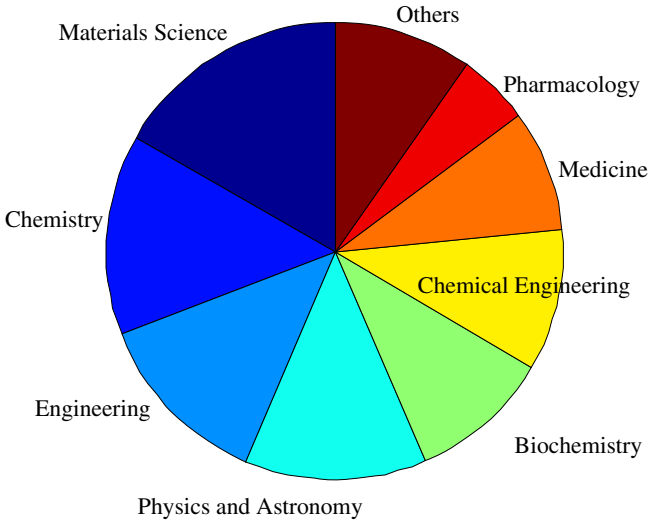


Fig. 5. Areas of silver nanoparticle studies in Malaysia.[43]

to this topic is 231. Universiti Putra Malaysia, University of Malaya, Universiti Kebangsaan Malaysia, and Universiti Teknologi Malaysia are the top four institutions publishing works on AgNP studies. The most studied subject area is materials science (see Figure 5). After 2010, publications on AgNPs significantly increased compared to the previous years. This is attributed to the establishment of NND and all the aforementioned institutes.

In Malaysia, applications of AgNPs are established for plastic (MEGACOLD 99.9% antibacterial nano-silver ice pack), water treatment (Olsmopure CLT33 Nano Silver GAC), and catalyst (mono nano silver powder). NSM, a company focusing on the AgNP production and application, has launched several products such as Electrode Colloidal Silver (ECS®) for disinfection of water, and products for beauty health, agriculture, life stock raising, and fish farming. Also, the company has a product called SilverSol™ for antibacterial application. These products clearly show that AgNPs are being heavily utilized for various purposes in Malaysia.

Although the Malaysian government has launched NND for the nanotechnology development, study of AgNPs remains a new field in Malaysia. To date, no official regulation by the government exists to monitor and control AgNP use in Malaysia. It is well established that AgNPs are widely used in household products, textiles, food containers, consumer products, and electronic devices. Also, other companies are beginning to focus on producing AgNPs in Malaysia. Hence, it is only appropriate that policies on AgNPs, from their synthesis until their utilization, are formulated and then issued by the government. This is essential to control and monitor AgNPs that possibly can inflict long-term damage to the environment because of their toxicity.

CONCLUSIONS

This paper has critically reviewed AgNPs from the perspectives of research trends, global consumption, synthesis, properties, and future challenges. Generally, there are three methods for synthesizing AgNPs, namely physical, chemical, and biological. The physical approach has several drawbacks, such as large space requirement, high energy consumption, and long time consumption to achieve thermal stability. The chemical approach provides an easy way to produce AgNPs although the toxicity of their by-products is a primary concern. Green synthesis of AgNPs is becoming more popular since it is environmentally friendly and cheap. The present review showed that AgNPs have desirable physical, chemical, biological, optical, thermal, electrical, and catalytic properties. These properties have the potential to be exploited in several applications. On the other hand, it is worthwhile to be aware that AgNPs are toxic, which must be considered when they are used in consumer products.

In green synthesis, the challenges that should be considered are simplicity, cost, and time consumption. Also, how this technique can be employed to produce shapes other than spherical is a matter worth exploring. AgNPs released into the environment should be clearly investigated, starting from their sources, mechanisms, and transportation to their effects, by means of better models than the existing ones. A continuous-flow tubular microreactor prototype is potentially an alternative for scaling up AgNP production. A study case in Malaysia revealed that, due to the high expansion of nanotechnology industry, especially those related to the AgNPs field, a proper set of regulations to handle the numerous issues should be in place as soon as possible.

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