Review Article

Optimized Synthesis Approaches of Metal Nanoparticles with Antimicrobial Applications

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Received 25 October 2020; Revised 2 December 2020; Accepted 4 December 2020; Published 22 December 2020

Academic Editor: Liliana Cristina Soare

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According to the literature data, metal nanoparticles can be synthesized by various methods but the chemical reduction methods are mostly applied getting more advantageous comparing with the other methods. This work emphasizes also that the combination of synthetized methods could lead to the spectacular results depending on the application. Among the chemical methods, this work analyzed the polyol method, radiolytic process, microemulsion method, solvo-thermal method, microwave-assisted synthesis, and electrochemical synthesis. It also presents the main application of metal nanoparticles in biomedical fields, empathizing on their antimicrobial potential.

1. Introduction

One of the earliest reports about nanomaterials dated on the nineteenth century, when Faraday prepared colloidal gold, named that time “divided metals.” Later then, the German microbiologist Robert Koch demonstrated that compounds with metal incorporated as gold inhibited the growth of bacteria. This discovery led to him the Nobel prize for medicine in 1905. This antibacterial particularity of the noble metals consequently of their nanoparticles was confirmed along the history, by using them, as antimicrobial additives in foods, food packaging, at the first stage, to ensure their quality, then their application were extended to the other sectors as medicine, water waste treatment, electronic equipment. In China, according to the traditional habits, to add a gold coin in cooking rice helps to replenish a deficit gold in the body. In Europe, Roman people use the silver coins for preservation of food and liquids. In India, Ayurveda system used the extremely fine powder known as “bhasma” which has been used for treatment against anemia, fever, asthma, sleeplessness, digestion, cosmetic application, etc. [1, 2].

Nanomaterials exist from the ancient times having natural or synthetic origins. Many materials exist in micro- or nanoscale, and their applications are developing exponentially, in the last time. The industrial world as resin processing or electronic or medical industry is also benefiting from the use of micro- or nanomaterials. The natural world produces nanoparticles and colloids such as volcanic ash, milk, or nanostructures such as the special surfaces of insect wings and leaves (Lotus effect being well known). Thus, the nanomaterials are not at all new, but they become interesting since the researchers were able to correlate their small dimension with the potential applications and their importance in our life [3].
Starting with the twenty-first century, the nanotechnology has become one of the most important research fields in physics, chemistry, engineering, biology, medicine, and industry. Nanoparticles include those particulate substances which have one dimension less than 100 nm, at least [4].

Nanoparticles having an important characteristic as a large surface-to-volume ratio and the size of their characteristics exhibit unique and differentiate physical, chemical, and biological properties relative to bulk materials and provide us many breakthroughs that will change the direction of technology [5–7]. Consequently, the properties of nanoparticles are deducted according with their structures. The transition from bulk to micro- and especially to nanoscale can lead to different changes. In fact, the stable interatomic bonding that exists in a large crystal is not found at atomic level surface so the atoms become more mobile and reactive. Such materials have high chemical reactivity and physical affinity such as to show specific physical, chemical, biological, electrical, optical, and magnetical properties [8].

The nanotechnology included the nanodevice with nanoelectromechanical system and nanomaterials. The last one can be divided in nanostructured polymers and nano-crystalline depending on the type of their atomic structures. The nanostructured polymers included the nanoparticles while the nanocrystalline includes the carbon nanotubes, fullerences, or quantum dots (Figure 1).

Thus, based on their physical and chemical properties, nanomaterials are classified in several main categories as:

(i) Carbon-based materials: the major representatives being fullerences and carbon nanotubes of which main application is for efficient gas adsorbents, for environmental remediation, as support for different inorganic and organic catalyst, drug carrier, imaging, etc. [6, 10]

(ii) Metal nanoparticles: are purely made of metal precursors and possess unique opto-electrical properties (Figure 2). Their faces, shapes, and sizes are very important according to the final application. Due to their optical properties, the gold and silver NPs are used for the preparation of the SEM samples, to enhance the electric stream, which helps in obtaining quality SEM images [6, 11], but there are a lot of medical applications, as we will describe later [12, 13]. Metal nanoparticles such as gold nanoparticles are used in optics or catalysis; silver nanoparticles due to the specific properties are especially used as a catalyst for chemical reactions, biomarker, biosensor, superconducting material, cosmetic products, and electronic devices

(iii) The porous nanostructured materials play an important role in bone growth by influencing the migration proliferation and differential of the cells. Mesoporous silica or microporous clays are extensively used in medical application, especially as drug delivery systems, biosensor, catalyst, pigments, thermal insulators, and the porous system being able to host a large amount of biological active agents which further can be released according to a proper profile [14, 15]

Metal oxides are extensively used in many applications; titanium dioxide is used especially as pigment, main component in air cleaning products; zinc oxide is used in ceramic as well as in biomedicine; selenium nanoparticles play an important role in biologic activity [16]. The most commonly studied materials are based on oxides including silica, ZnO, Fe2O3, and TiO2 phosphates and especially calcium phosphates and metals [17].

Nonmetallic, polymeric composite materials with nanoparticles are being used increasingly widely in aviation technology (AT), showing improving features to the structural materials operating under different natural conditions.

Discoveries over years mainly in the last years have demonstrated that the electromagnetic, optical, and catalytic properties of noble metal nanocrystals are strongly influenced by shape and size. Besides improvement of the physical properties, the metal oxide nanoparticles have good antibacterial activity such that the antimicrobial formulations could be effective bactericidal materials [18, 19].

In preparing this paper, it was used as EndNoteX9 software, as a main source of documentation of ISI Knowledge. For documentation, it is focused for recent articles, publications, and books, using the following keywords: silver nanoparticle synthesis, silver antimicrobial effect, and nanoparticles applications. This review presents comprehensive information on the synthesis of AgNPs by various methods and the antibacterial effect of AgNPs applied in different activity domains. In addition, the review focuses on the antibacterial effect on human healing and various substrates with the protective role against biofilm formation.

2. Physical and Chemical Characteristics of Metal Nanoparticles

The ultrafine size of nanoparticles itself is one useful function. Thus, the fine particles are able to be absorbed more easily through the biological membrane and could be delivered selectively through enhanced membrane to certain affected cells. This ability is due to the large specific surface area of the nanoparticles which is an important characteristic which modifies reactivity and solubility, sintering performance, related to the mass [20].

Due to high surface-to-mass ratio, natural NPs play an important role in the solid/water partitioning of contaminants which can be absorbed to their surface, coprecipitation of contaminants, or trapped by aggregation of nanoparticles (NPs). The interaction of contaminants with NPs is dependent on the characteristics, such as size, composition, morphology, porosity, and aggregation/disaggregation structure. Based on these characteristics, the removal of heavy metals from contaminating water by photodegradation is based on the high surface area of NPs due to the very small size (<10 nm) [6].
The electrical properties of nanoparticles are a consequence of atomic structure keeps at nanostructure level which reveals at different electronic applications. Nanoparticles which are included in crystalline matrix cause a large charge carrier concentration without strongly influencing their mobility. Nanomaterials contain grain boundaries which are efficiently spreading in mass as mid- and long-wavelength phonons, thus reducing the thermal conductivity [7]. The electrical properties of nanomaterials are highlighted by the 1D structure which conduct electrical current different by the bulk material due to the size and organized structure of nanoparticles which improve the electrostatic potential enable to use a low turn-on voltage for field emission [21].

Catalytic properties—the nanoparticle due to their shape—could speed up the chemical reaction through a provision of new reaction path of lower activation energy or provision of a surface to which the chemical reactants can adhere and react more readily then. This property is useful especially in biomedical applications as seed vapor-liquid-solid process or deposition of both carbon nanotubes and nanowires [22]. The improvement of catalytic activity by tailoring of certain facets of crystalline surface of nanoparticles makes them a suitable proposal to solve the various technological problems [23]. The large surface area of AgNPs provides more possible reactive sites and high surface energy, making the ideal candidate [3].

The mechanical property effects of nanomaterials in thin film were studied to improve the properties of different materials by incorporating the thin film with nanomaterials. The size of nanomaterials must be less but the properties must

**Figure 1:** Various types of nanostructures [9].

**Figure 2:** Various colors of AgNP synthesized example based on plasmon resonance.
be much better than in the bulk. Thus, the nanomaterials have distinct mechanical properties as a result of shorter bond lengths which lead to improve the quality of material, being stronger and stiffer, and limited size of the units of material diminishes the defects of materials [2]. The modulus elasticity, hardness, movement law, and friction are improved by NPs in which characteristics are given by the size of them [6].

Magnetic properties are given by the NP size less than 10-20 nm. The magnetic properties are given by uneven electronic distribution [6]. Magnetic properties of nanoparticles depend strongly on their size and nanostructured material, showing that the single-domain system is energetically favorable. Thus, the nanomaterials can be classified according to the type of interaction among the magnetic particles in from no interaction in well-distributed nanoparticle to strong interaction nanostructured system [21].

Among the noble metals studied, synthesized, and applied in electronics area are gold and silver NPs. The characteristics such as high thermal, the electrical conductivity, and the relatively low contact resistance quality AgNP as one of the most promising materials in electronics [3]. Silver nanoparticles have the highest thermal conductivity among all metals, resulting in the use as conductive fillers of conductive adhesives and thermal interfacial materials in electronics. Silver nanoparticles are widely used in the electronic fields [24].

The thermal properties showed by nano fluids in water or different solution such as ethylene exhibit advance thermal conductivity through enlarging surface area caused by heating the system which transfers the energy and takes place on the surface of particles [6, 25]. The thermal conductivity, specific heat, and melting point are strongly dependent on the particle feature size of nanomaterials [21].

Optical properties similar with the electrical ones are influenced by the bandgap size; the shape and smaller size result in a larger energy difference between neighboring discrete energy levels. Thus, the smaller particles have shorter wavelength in the absorption spectrum, and the color shifts are from red to blue [4].

Surface plasmon is an oscillation of electric density in the conduction band that occurs at the metal/dielectric interface. As stronger is the amplitude of oscillation as much roughness is the surface of the metal nanoparticle surface. The information about the structure of nanoparticles is given by the surface plasmon (SP). It is known that the peak wavelength of localized surface plasma resonance (LSPR) spectrum is directly dependent by the physical properties such as the size, shape, and interparticle spacing of NPs, dielectric properties solvents, and adsorbents [6]. The optical properties of the metal NPs such as noble metals can be tuned according to the size and shape, in all the visible region based on plasmon resonance [3, 6, 26].

Photocatalytic properties or hydrogen production represents an opportunity for the cleaning effect and sustainable and renewable energy system. Nanoscience has opened by nanotechnology a new field of nanostructured photocatalysts with a large area for optimized light absorption and minimized charge carrier transport. The TiO₂ nanoparticles have received more attention being more stable, corrosion-resistant, nontoxic, and cheap [27].

Nanoparticles find a diverse application in medicine, biology, and industrial technology. Their specific properties are effectively used in chemical reactions such as biomarkers, biosensors, cryogenic superconducting materials, cosmetic products, treatment of wastewater, textiles industry, and construction field [28]. Based on the nanotechnology development, there is a potential of providing novel ways regarding the treatment of diseases which were antecedently tough to focus on due to size restrictions [29]. For medicine, it is important to create application by considering biofunctional nanoparticles, and there are many ongoing types of research in developing technologies, materials, and devices for the patient well-being [29]. The nanosize plays an important role in the biotechnology that makes it more prolific for all of their biological applications. The silver nanoparticles are used in the treatment of different diseases interrelated with microbes and discharge the silver ion in the deactivation of cellular-based enzymes delayed penetrated membranes. The antibacterial activities given by the AgNPs can use it in the HIV infection treatment with double action at the initial phase of viral duplication and later phases of the HIV life cycle [30–32].

A major trend in the research laboratories is to design and manufacture nanostructured systems with improved physico-chemical properties for catalytic applications. The recent discoveries on the improved technological performances are getting by coupling different nanostructured materials offering to the final products an improved properties [33].

The using of nanoparticles as a solution to preserve the architectural buildings, monumental elements, and artistic items is a great opportunity increasing nowadays. Titanium dioxide (TiO2) is among the most important and widespread nanostructured product used for renovating buildings by its mainly photocatalytic effect. Based on its photocatalytic property activated by solar light, the titanium dioxide nanoparticles can be used to protect the surface of stone buildings and architectural monuments [34]. The unique physiochemical properties combined with the high inhibitory capacity of nanoparticles have led to antimicrobial applications [23]. Other metal oxides are known to possess antimicrobial property as silver or zinc oxide nanoparticles [35, 36].

The bioactivity of metal nanoparticles is resulting from the interaction with various constituents of the immune system, and many studies have demonstrated that the morphology of nanoparticles leads to the desirable effect [37]. Due to the biological activity of metal nanoparticles, a growing interest is highlighted for these nanoparticles especially because of their potential application in medicine, pharmacy, biomedical applications, industry, etc. [38].

Since ancient times, silver has been used extensively for many applications, not only in medicine or alternative medicine but also in jewelry industry, metalcraft, photography, vessels, or containers for liquid due to its antimicrobial properties. Actually, it is also used in electronics, optoelectronics, catalysis, imaging, or biomedicine. Some of the most important applications of AgNPs are related to their antimicrobial
activity against several bacteria, fungi, and viruses (over 650 strains) consequently widely used as antimicrobial agents for textiles, cosmetics, medical devices, mobile phone, refrigerators, and filters [5, 39].

Nanoparticles showed a high antimicrobial activity against various bacteria. The antimicrobial activity of nanoparticles can serve as transducers under different stimuli (as heating, UV or visible radiation, etc.) into another form of stimuli. These characteristics are very useful in application of medicine or biology area. Due to these characteristics, the bacteria can be damaged or even killed due to the reactive oxygen species (ROS) production [40, 41]. Moreover, the mechanism of action on the bacteria or film is still in research. As the mechanism of action of bulk antimicrobial particles is still not clear, we assume a part of the action mechanism of nanoparticles still unrevealed.

The antibacterial effectiveness of nanoparticles results from their maximum contact capacity with the surrounding medium. This effectiveness is owed to the large number of particles developed on the surface and their shapes [42].

The antibacterial property of silver nanoparticles has opened up a number of opportunities for medical treatment; the textile treatment or surface treatment all lead to the healing and the protection of the human body. Due to these properties, the silver nanoparticles have opened new horizons towards novel approaches in many domains [43].

According to the results of microbiological test, the silver NPs noticed a highly antibacterial effect against Escherichia coli and Staphylococcus aureus. It is important to notice that in the form of powders or suspensions, due to the high surface to volume ratio, AgNPs have been used as antibacterial; the main advantages of using AgNPs are related to low toxicity, high efficiency, and low risk of developing resistance and reasonable production cost [38].

The mechanism of action of AgNPS is described as an electrophile. The silver nanoparticles interact with microorganisms, and probably the modified factors from the surface of interaction the silver ions (Ag⁺) are released, and these ions may affect and damage the microorganism. These silver ions could attach the negatively charged cell walls of microbes to deactivate cellular enzymes and disrupt the membrane permeability (Figure 3); consequently, cell lysis and cell death occurs. Moreover, in the broad spectrum killing and lesser possibility to the development of microbial resistance comparing with other metal nanoparticles, it might possible that AgNPs achieved the highest level of commercialization (more than 50% from the total sales of nanoparticles). Consequently, the interest for nanosized silver particles was rise up much more when the dependent relation between size and shape has been highlighted [5].

The aim of the silver nanoparticle synthesis is mainly to obtain and stabilize the silver nanoparticles with antimicrobial performance. There are few differences in the researchers’ opinion related to the shape and size of nanoparticles which are given the biocidal activity. Some of the researchers reported that the anisotropic shapes of silver nanoparticles, such as nanoplates or triangular nanoprisms, led a key role to achieve the high biocidal activity. For example, it was shown that the truncated triangular AgNPs exhibited better antibacterial efficiency than that of spherical and rod-shaped silver particles [44, 45]. In same way, it is also described that the silver nanoplates demonstrated higher antibacterial effectiveness than silver nanorods or nanospheres [46–48]. One of the explanations for the great antibacterial activity of these anisotropic-shaped AgNPs was the basal plane with high-atom-density (111) facets which acted as the maximum reactivity sites leading to the strongest antibacterial activity [5]. On the other hand, some works indicated that the spherical shapes demonstrated a high bacterial effectiveness sustained by the spherical shapes, which provided the maximum reactivity and stability to obtain the highest antibacterial effectiveness [5]. Depending on the nanoparticles, application is searching the maximum effect by the combination of their size and shape of nanoparticles.

The nanoparticles smaller than 25 nm can be easily internalized into cells by passing through cell membranes, initiating a cascade of a subsequent biochemical process. However, nanoparticles of all sizes can also have antibacterial effects without entering the cell, including disruption of the cell by binding to its surface, dissolution, and release of free metal ions that can be transported into the cell [49].

Nanostructured silver has a broad spectrum of antimicrobial activity and acts against of both Gram-positive and Gram-negative bacteria and many other strains. The antibacterial activity of the silver nanoparticles was investigated for both Gram-positive and Gram-negative bacteria. The inhibition for both bacteria was noticed [50]. Nanosilver also has antifungal activity and could inhibit a large number of ordinary fungal strains [3, 51, 52].

Due to the microorganism colonization of different substrates, water-based products used in medicine, industrial, food, and cosmetics and because of emergence and increase in the number of multiple antibiotic-resistant microorganisms, many scientists have developed methods for producing new antimicrobial products such as to overcome the resistance of microorganisms [53].

Silver nanoparticles have been proven to have an oligodynamics effect, thus could enhance the development of nanotherapeutics application [32]. The application of nanotechnology in biomedical world has led to the novel prospective engineered nanomaterials for drug formulation, targeted drug delivery, gene therapy, and so on. As novel materials used for this purpose are nanoparticles of metals with different shapes, each of them has specific application and efficiency. The advantage of nanoparticles used in stroke therapy gained an important role by protection of agent degradation, decreasing the risk of exposure to nontarget tissue when tissue selective NPs being used, by providing a protective shell for encapsulated contents, and by keeping a high intra-particle drug concentration, thus increase the efficiency across the blood-brain barrier [54].

Nanosilver applications were encouraged in medicinal area because of their anti-inflammatory effects and the ability to promote wound healing. AgNPs due to the antimicrobial activity are used in orthopedics and dentistry as additives in bone cement, coatings of implants for joint replacement, and intramedullary nails for bone fractures and additive in polymerizable dental materials [55].
Nanosized particles have drawn increasing interest in the medical application of every branch due to their ability to deliver drugs in optimum dosage with the increased therapeutic results efficiency [6]. The photothermal therapy is based on the optical properties of NPs; superparamagnetic properties of NPs can be used in treatment of tissue-repair, detoxification of biological fluids, and drug delivery to the affected cells as well as to the cell separation [6]. Various polymers used in developing biodegradable NPs led to the new drug generation with high efficiency. The silver nanoparticles showed an enhancement of antibacterial activity and long-lasting disinfectant effect [56, 57].

The size of nanoparticles has a direct connection with their application. In biomedicine, the most effective parameter which affects the toxicity is the size of the nanoparticles, and, sometimes also, the shape or the stabilizing agent can be very important. The nanoparticles could penetrate the cell membranes and go directly to the circuit blood and organs and the larger particles cannot access the nanoparticles. Thus, the same nanoparticle capped with different compounds can have toxic or nontoxic activity. The result of nanoparticle integration in the field of medicine has led to their application mainly in targeted drug delivery, imaging, sensing, and artificial implants [23]. The studies about the sizes of nanoparticle have also extended in industrial application. The small size of metal nanoparticles has been demonstrated that have higher efficacy than bigger ones [58].

Nanosized particles have been used as agent delivery to the retard multiplication of cancer cells. These nanoparticles if they are coated with a special shape as the carbon nanotubes were noticed that act as the reinforcement network and helps the drug to be delivered directly on the affected cells [54].

Shape-dependent optical activity of the metal NPs has brought a revolution in the field of bioimaging and diagnosis. Together with AgNps, the gold nanoparticles such as nanoshells, nanocages, and spherical shapes show an effective photothermic destruction of cancer cells and tissue. The NP size plays a key role in their long circulation, biodistribution, and clearance [43, 50].

The antiviral properties of silver nanoparticles become the strongest candidates as antiviral agents. The viral disease depends on the entry and attachment of the virus onto the host cell binding of viral surface components with ligands and proteins on the cell membrane. Thus, the new antiviral agents were to interfere with the interactions of virus ligand and cell membrane to block the attachment and entry of the virus into cells [32]. The antiviral activities of silver nanoparticles could lower the risk infection or might as well prevent an epidemic viral disease as COVID-19 [32, 59, 60].

The shape of nanoparticles could influence their biocompatibility and toxicity. In medicine, for example, the spherical particles are more internalized than the elongated shape particles lying parallel to the cell membrane [28, 61]. On the other hand, the nanorods or nanoprisms shapes [62](Figure 4(a)) of

Figure 3: Schematic representation of toxicology effect of multifunctional nanoparticles (NPs) in bacterial biofilms.
metal nanoparticles have been demonstrated that have more efficacy than the spherical shape (Figure 4(b)) of same nanoparticles [18]. Thus, depending on the application area and desired results through the certain synthesis, the right shape and size of nanoparticles can be controlled.

The surface charge of nanoparticles is another important factor that can affect biocompatibility in medical applications. The zeta potential of nanoparticles in solutions is \( \pm 30 \text{ mV} \) which leads to good stability and prevents the agglomeration of the particles. The cationic nanoparticles are more active than the neutral or anionic nanoparticles [28].

Shape and size control of nanoparticles are promising parameters which can tailor their physical and chemical properties for various application in industry, medicine, biotechnology, electronics, and so on. The complex structures of nanoparticles exhibit superior physical and chemical properties. Consequently, depending on their structure, the surface plasmon resonance (SPR) band corresponds to dipole or quadrupole plasmon resonance, but only one or both can be observed in a certain structure. Another characteristic that might be valuable to the nanoparticle is their stability. Stability of nanoparticles and use of environmentally friendly chemicals are other considerations for large-scale applications [9].

A major feature that discriminates against various types of nanostructures is their dimensionality. The shape of nanoparticles is a factor governing other properties as the aspect ratio, porosity, the surface roughness all have direct influence to the surface-to-volume and consequently their properties [21]. The nanoparticles with 0D have uniform particle arrays (quantum dots), heterogeneous particles, and separate, core–shell dots, hollow spheres or nanolenses; they have nanometer feature size in every direction [21]. These nanoparticles are used in solar cells, single-electron transistors, and lasers products [63].

The 1D nanoparticles compared with 0D nanoparticles materials have nanometer size in two directions while one dimension can reach even centimeter length. They are used for ideal systems consequently having a wide range of potential applications. They also have strong connection with electronic, optoelectronic nanoscale dimensions, and nanoelectronics. The nanowires, nanorods, nanoprism, nanobelts, or hierarchical nanostructures are representative types of 1D [63].

Two-dimensional nanostructures, owing their low dimensional characteristics, different than the bulk properties, have exhibited a unique shape-dependent characteristics and subsequent utilization in building blocks for the key components of nanodevices. The 2D nanoparticles are used for investigation and developing of novel applications in photocatalysis, nanoreactor, and nanocontainer products. Their structure can create a continuous island as films therefore are used in novel applications [63]. They have thin sheet aspect.

Three-dimensional nanostructure materials have potential applications, owing to their large specific surface and other superior properties over their bulk counterparts from the quantum size. The 3D nanostructures are used in the area of catalysis, magnetic material, and electrode material for batteries. On the other hand, such materials with porosity in three dimensions could lead to better transport of the molecules. Therefore, this kind of 3D nanoparticles is intensively used in biomedicine in nanocomposite materials or in drug compounds [63, 64].

The nanoparticles raised plenty of interests from both fundamental science and technological applications owing to their physical, chemical, and magnetic properties highly improving the characteristics from higher dimensional counterparts. Therefore, many techniques have been developed to synthesize and fabricate with controlled size, shape, and dimensionality [63, 65].

### 3. Synthesis Routes of Nanoparticles

The methods used for nanoparticles obtained are different even which are physical, chemical, biological, or combination between them; the final characteristics of products are important such as to fully reply to the requirements. The methods used for synthesizing nanoparticles can be framed in two main ways: top bottom approach and bottom down approach [32](Figure 5).

The principle of the top bottom synthesis is to take a bulk piece of material and then modify it into the wanted nanostructure and subsequent stabilization on the resulting nanosized metal nanoparticles by the addition of colloidal protecting agents [66].

The top-down or top-bottom (Figure 5) approach involves the use of bulk materials and reduces to the nanoparticles by the way of physical, chemical, or mechanical processes. As a figurative aspect, this method is similar to breaking the wall down into its components [67]. In this approach, it is starting from larger structures, which decomposed into smaller units until reaching the desired size [6].
For this method, a mechanical energy, high energy lasers, thermal, and lithographic methods are usually used for nanoparticle production. As examples, these categories include atomization, arc discharge, laser ablation, electron beam evaporation, focused ion beam lithography, vapor condensation, condensation in inert gas, and electrodeposition [66, 67].

The physical methods, such as evaporation-condensation, laser ablation, and electron beam evaporation processing, are included in top-down synthesis. The absence of solvent contamination during the preparation of nanoparticles is one of the main advantages of these physical methods. The ball milling method is to put the milling balls and metal materials with a certain ratio and inert gas milling at a time, with a rotating speed. Depending on these factors, the certain size of nanoparticles is obtained [68]. Beyond this, the agglomeration effect is often a real challenge of these methods, because capping agents are not used [19]. Comparing with the chemical reduction using the high temperature or pressure, there are some disadvantages which consume a great amount of energy while raising the environmental temperature around the source material and requires a lot of time to achieve the thermal stability [66, 69, 70].

The bottom-up synthesis refers to the construction of a structure atom-by-atom, molecule-by-molecule, or cluster-by-cluster. This is similar to building up “the brick” from raw materials. This approach is employed in reverse of NPs which are formed from simpler substances; therefore, this procedure is calling building up approach. Examples of these cases are sedimentation and reduction techniques which includes sol-gel, green synthesis, spinning/spraying, and biochemical synthesis [6]. Colloidal dispersion used in the synthesis of nanoparticles is a good example of bottom-up synthesis (Figure 4) [66, 67].

Bottom-up synthesis of nanomaterials is divided into various categories: gaseous phase, liquid phase, solid phase, and biological method. Wet chemical, liquid-phase reduction is the most frequently applied method for the preparation especially the metal nanoparticles [66]. The reduction (Equation 1 Reduction of silver salts) of the corresponding metal cation represents a straightforward reaction to obtain metal nanoparticles. Generally, these reactions have common steps as in the solution characteristics: reduction, nucleation, growth, coarsening, and/or agglomeration are specific to this synthesis procedure [67, 68]. Many methods are suggested for chemical synthesis of silver nanoparticle formation: chemical reduction method, polyol method, radiolytic process, microemulsion method, microwave-assisted synthesis, and electrochemical synthesis have been developed for metal nanoparticle synthesis [71]. For chemical synthesis, there are two essential steps: nucleation and growth nanoparticles. Both steps are influenced by different parameters as temperature, pH, concentration of reaction components, reducing or stabilizing agents, and molar ratio of surfactant/stabilizer and precursor (Equation 1 Reduction of silver salts) [19].

The most common method is used in synthesis of metallic NPs in aqueous solution or organic solvent by reducing metal salts [19].

\[
\text{Reduction of silver salts : } m\text{Me}^{a+} + n\text{Red} \rightarrow m\text{Me}^{0} + n\text{O}_{x}.
\]

(1)

This process usually employs three main components such as metal precursors, reducing agents, and stabilizing/capping agents. The advantage of the chemical synthesis of nanoparticles are the ease of production, able to get the right shapes, low cost, low impurity, thermal stability, and high yield; however, the use of chemical reducing agents can be harmful to living organisms [72].

Comparing with physical methods that demand sophisticated equipment(s), the chemical methods that are frequently used for synthesis of nanosized silver nanoparticles
include chemical reduction, microemulsion, photoinduced reduction, microwave-assisted synthesis, and solvothermal reduction [5, 73].

The AgNP is considered as a hybrid substance constituted by Ag\(^+\) aggregates and the capping agent of organic nature whose function is to stabilize the inorganic particles. The antimicrobial activity of AgNPs depends on how the core is formed and how its surface is stabilized with different anions. Thus, the way of AgNPs obtains imprint to the nanoparticle different physical, chemical, biologic, and optical properties. The possibilities of AgNP surface to interact with stabilizing agents are depending on their nature; thus, the capping agent can supply new properties of nanoparticles as surface charge, acidity, or basicity in function of pH and susceptibility to ionic strength; consequently, capping agent affects the antimicrobial properties in positive or negative way [38].

Therefore, they are many synthesis routes of AgNPs by chemical, physical-chemical, and green methods looking to get the best properties of nanoparticles used in different sectors. Using the AgNPs as antimicrobial agent in surface coatings opened the way of antimicrobial treatment, especially for the solid substrate [74]. In addition, epoxy coatings containing antimicrobial nanoparticles offer a significant barrier protection of surface avoiding the growth of bacteria, microorganisms, and fungus [51].

The chemical routes lead to the obtaining of specific nanoparticle shapes which gives the antimicrobial efficiency. Chemical reduction is the most frequently easiest way for the preparation of silver nanoparticles as stable, colloidal dispersions in water or organic solvents. The reducing agents are, mainly, sodium borohydride, trisodium citrate, and elemental hydrogen. The reduction of silver ions (Ag\(^+\)) in aqueous solutions generally following the Turkevich method leads to the silver particles with the diameters of several nanometers. The reduction of various complexes with Ag\(^+\) ions leads the formation of silver atoms, which followed by agglomeration into oligomeric clusters (Figure 6) [68]. These clusters may lead to the formation of colloidal silver particle. When the silver nanoparticles are much smaller than the wavelength of visible light, these solutions have the yellow color with an intense band in the 380-400 nm range and other less intense or smaller bands at longer wavelength in the absorption spectrum [66]. Controlled synthesis of silver nanoparticles is based on a two-step reduction process. In this technique, a strong reducing agent issued to produce small silver particles which are growing in the second stage by further reduction with a weaker reducing agent. Reducing agents such as sodium borohydride (NaBH\(_4\)) or hydrazine (N\(_2\)H\(_2\)) and formaldehyde (CH\(_2\)O) lead to small particle shape formation in the first stage [65–67].

The nucleation phenomena appear when the solution is supersaturated, and the reduction and nucleation rates are slower. In this step, the AgNP solution has the predominantly yellow color, thus indicating a spherical shape of nanoparticles. The growth phenomena are explained by agglomeration/diffusion of metal atoms [75]. The surfactants have the stabilizing role agents, and they prevent the aggregation of the nanoparticles. The surfactant will reduce the reactivity of the precursors and reduce the rate of the reduction process. The stabilizing agent ensures the formation of metal-surfactant complexes in the reaction solution. This phenomenon implies the development of the nucleation process. Furthermore, the adsorbed stabilizer ions will create electrostatic repulsion between the coated nanoparticles, thereby increasing the stability. This is essential for narrow size distribution of the particles [75]. Knowing the principles of reduction wet chemical mechanism, we can estimate better the type of reactants we can use in the silver nanoparticles [76].

Using a strong reducing agent such as sodium borohydride, ethylene glycol, or ethanol, the reaction must lead under the various conditions such as to obtain the silver nanoparticles. The quantity of reducing agent and condition of reaction must be carefully selected such as do not produce the agglomeration of nanoparticles. Usually, at this chemical reduction, in order to protect the silver nanoparticles, several capping agents with the protective surface characteristic are used. A variety of chemical methods have been developed for the preparation of different silver nanoparticles in solution [66].

From literature, there are many possible combinations of reducing and stabilizing agents that can be used in order to allow a reliable way manufacturing of AgNPs with certain characteristics. Glucose used as reducing agent in AgNP synthesis allows obtaining spherical shape NPs with slightly uniform size having a superior antibacterial action [68, 77]. Glucose nanosilver colloids are biologically compatible and have the potential to be used in medical and pharmaceutical applications [66]. Ethylene glycol has higher antibacterial activity than glucose, but according to SEM results, it was noticed that the capping effect is not performant comparing with the glucose. Sodium borohydride is a strong reducing agent and is used in ice-bath, the nanosilver synthesis. The obtained solution has the yellow color first time; then, the solution has violet or grayish color; after which, the colloids break down and particles settle out. The quantity of sodium borohydride (Equation (2) Borohydride-based reduction reaction of silver salts (NaBH\(_4\)/Ag\(^+\)) is 1 : 1 but NaBH\(_4\) is usually added in excess in order to prevent the flocculation phenomena [78]. The extra borohydride anions remain in solution helping to stabilize the formed nanoparticles, but it also begin to hydrolyze decreasing the available borohydride ion [66, 67].

\[ \text{Borohydride – based reduction reaction of silver salts : } \text{AgNO}_3 + \text{NaBH}_4 \rightarrow \text{Ag}^0 + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{B}_2\text{H}_6 + \text{NaNO}_3. \]

(2)

Aniline as a reducing agent is a relatively milder reducing used for the reduction of silver ions. The sizes and shapes of nanosilver obtained with aniline in presence of C\(_{12}\)TAB (cetyltrimethylammonium bromide) are roughly spherical with ranges between 10 and 30 nm [66].

Ethanol used as reducing agent uniform silver nanoparticles can be obtained at a temperature of 90°C, under atmospheric conditions in presence of linoleic acid and sodium
linolate. Silver nanoparticles have average diameter of 12 nm [66].

Tri-sodium citrate as reducing agent is used at boiling temperature during silver nanoparticle synthesis. The reaction (Equation (3)) allowed taking place until color changed to greenish-yellow solution. The particles are in broad size distribution from 15 to 60 nm with average size of 40 nm, as a consequence of the slow rate in the citrate reduction method. The sodium citrate acts as reducing as well as stabilization agent [38, 66, 67, 78]. Moreover, it was confirmed that using the tri sodium citrate in chemical synthesis of silver nanoparticles, the solution was transparent and stable over time (at least 3 months) [62].

Chemical reaction of silver salt with trisodium citrate: $$4\text{Ag}^+ + \text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot \text{H}_2\text{O} \rightarrow 4\text{Ag}^0 + \text{C}_6\text{H}_8\text{O}_7 + 3\text{Na}^+ + \text{H}^+ + \text{O}_2$$.

The reduction of silver salts with different reducing agent such as (Na$_3$C$_6$H$_5$O$_7$) trisodium citrate or sodium borohydride in presence of capping agent such as polyvinylpyrrolidone PVP in various concentration and condition of reaction (temperature or pH) leads to obtain a various shapes of nanoparticles especially the spherical shapes which has high antibacterial activity compared with triangular shapes of same nanosilver particles [5]. The specific shapes and sizes of nanoparticles lead to different colors of solution with UV absorption wavelength (Figure 7) at various values depending on their shape and sizes.

Using organic solvents in AgNP synthesis has some advantages such as high yield and narrower size distribution; besides, in some cases, the solvent itself can act as reducing agent in AgNP synthesis. Polyol method can be also considered as a case synthesis in organic solvent; the versatility that provides to obtain AgNPs with different morphologies makes this method relevant to be considered. Polyol synthesis is a reduction of metal salt used as precursor, usually ethylene glycol (EG) or polyethylene glycol (PEG) at temperature, and as a capping agent in order to prevent agglomeration is used PVP (polyvinylpyrrolidone). EG (ethylene glycol) or PEG (polyethylene glycol) probably oxidizes to aldehyde species. The reduction power of ethylene glycol (EG) as well as PEG (polyethylene glycol) is markedly dependent on the temperature, giving the ability to control the nucleation and growth process by choosing temperature [67].

The polyol method is able to obtain AgNPs with different morphologies making this method relevant to be analyzed separately [67, 79]. Polyol synthesis is an excellent method for the production of metallic nanoparticles. Based on this method, a lot of silver nanoparticles with different shapes and sizes have been obtained by variation of reaction condition [80]. Using polyol method with a certain EG or PEG/PVP ratio, controlling the pH by adding ammonia could lead a good size control and well dispersed of Ag nanoparticles. The average particle size can be varied from 10 to 80 nm with a narrow distribution by controlling of capping agent and ammonia added [62, 81].

The hydrothermal synthesis using the polyol method is a green way which we can get different shapes and sizes of nanoparticles by controlling of temperature of reaction, pH or molar ratio between capping agent/metal salt. By this method, it can be controlled the sizes and shapes of nanoparticles. In the liquid-phase methods, it is necessary to select carefully the proper concentration of reaction components, the temperature profile, and time of reaction. The selection of chemicals needs to take into account the compatibility terms of solubility/polarity and reactivity of different components such as to avoid the unwanted by-products [7]. Based on this method, we can obtain a controlled size of spherical shapes of nanosilver particles by keeping a molar ratio as well as a temperature of reaction [82]. The hydrothermal method can be implemented in various options such as hydrothermal-microwave, hydrothermal-ultrasonic, hydrothermal-electrochemical, and hydrothermal-sol-gel [83].

Green synthesis of nanoparticles is a new aim of researchers to find less poisonous and hazard nanoparticles comparing with chemical synthesis. Green synthesis is an environmentally friendly approach providing nanoparticles with the low toxicity [84]. Chemical synthesis results in the presence of various solvents mostly noxious that are absorbable on the surface and have an adverse effect in medical application. Green synthesis makes use of environmental friendly, nontoxic, and safe reagents such as microorganisms, enzymes, fungi, bacteria, and yeast plant extracts that lead to eco-friendly nanoparticles. The extracts from different parts

![Figure 6: Representation of the nucleation and growth mechanism for AgNPs obtained by the citrate method.](image-url)
of the plants could be used in silver nanoparticle synthesis especially for medical applications with less toxicity [85]. Plant-mediated synthesis of silver nanoparticles is preferred due to the availability and their metabolites [73]. The reduction agents in the case of green synthesis are the enzymes which contain alcohols, flavonoids, alkaloids, and phenolic compounds which may contribute to the reduction of Ag⁺ [68]. The green synthesis method brings safe and eco-friendly nanoparticles, but on the other hand, the method is very slow, takes it a long time, and no shape well-controlled [86]. Due to the weak activity and low purity of eco-friendly chemicals, the reaction and baking times strongly affect the preparation efficiency in obtaining small size of silver nanoparticles [87].

4. Conclusions

Nanotechnology offers a great promise for the environment and technology and is able to revolutionize many problems that our modern society is facing, globally. Nanotechnology for green innovation aims for products and processes are safe, energy efficient, reduce waste, and less greenhouse gas emission.

Nanomaterials based on techniques and devices are on the big drive worldwide. The properties of nanomaterials are inserted in various technology components to be exploited at high performance. Surface modification and macroscopic manipulation of these materials could provide effective ways to take full advantage of the unique physical, chemical, and electrical properties. Their application in electronic field, as mechanical devices, optical and magnetic components tissue engineering, and other biotechnologies could develop the present and future technology. Nanoparticles by controlling their morphology and sizes are able to create biosystems. Thus, nanomaterials provide opportunities to advance human welfare, improving the medical devices used for human health, developing the revolutionary drugs for health, developing energy storage, and catalyzing photovoltaic energy conversion with industrial application.

Knowing the various synthesis methods with different precursors under different condition could lead a predictable certain shapes and sizes of nanoparticles. Different methods are used for nanoparticles obtained, and combination between the physical-chemical and biological synthesis provides a new possibility of conveniently synthesizing the NPs such as to obtain monodispersity, stability, desired shape, and size of particles which are the main requested characteristics.

Nanotechnology by the miniaturization of materials and improvement of their properties has multiple benefits for medicine, biology, cell phones, electronic circuits, energy storage, metallurgy, and construction area. Materials made with carbon nanotubes can be light and very resistant. Components and chips can now be made with features in the size of nanometers with high benefits. Titanium oxide nanoparticles used in construction materials have the air cleaning effect under light rays. Conceptual nanotechnology implies scrutinizing the world from the viewpoint of the atom or molecule. More advanced understanding at the nanoscale should finally allow creating artificial energy collecting systems, thus solving the existing penury of energy.

The application of NPs in electronics is based on their controlled shapes, structural, optics, and electrical properties which lead to a mixing synthetized types of nanoparticles.

Application in mechanical industries of NPs is based on an important property of nanoparticles such as the lubricated contact area could provide a very low friction and wear. This property is enhanced by using a certain shape of nanoparticles.

Science and technology research in nanotechnology making a cross linking between disciplinarity using the knowledge and transfer the information from the bulk to the nanoscale such as to get the materials in manufacturing, nanoelectronics, medicine and healthcare, energy, biotechnology, information technology, and national security. It is widely felt that nanotechnology will be the next industrial revolution.

Nanoparticles such as silver, gold, zinc oxide, and titanium oxide can be used for medical devices or included in
drug medicine for cancer therapy or in textile application against wounds or for water treatment and purification. The nanoparticles are integrated in our life and become step essential, through vital components, integrated into the human life and the industrial area.

The silver nanocrystals are very famous for their optical properties and are highly investigated for different applications. Their unique structural, optical, and electrical properties make them very useful in industrial area. Silver nanoparticles have been investigated and developed for antimicrobial application, and consequently, their applications in medicine, biomedicine, industries, construction, and other fields are increasing.

Nanoscience brings in front of the researchers new temptations by their varieties of synthetized types and combination which lead to various shapes and sizes of nanoparticles. That makes the nanoparticle application to get a deeper knowledge about their behavior, consequently to be used at the large scale. Thus, through nanotechnology, functional materials and devices in nanometer scale have been created, with wide application from human health to electronics area.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The work has been funded by the Operational Programme Human Capital of the Ministry of European Funds through the Financial Agreement 51668/09.07.2019, SMIS code 124705.

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