

Exploring the Effect of Operational Factors and Characterization Imperative to the Synthesis of Silver Nanoparticles

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Abstract

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The synthesis and application of silver nanoparticles are increasingly becoming attractive. Hence, a critical examination of the various factors needed for the synthesis of silver nanoparticles as well as the characterization is imperative. In light of this, we addressed in this chapter, the nitty-gritty on the operational parameters (factors) and characterization relevant to synthesis of silver nanoparticle. The following characterization protocols were discussed in the context of silver nanoparticle synthesis. These protocols include spectroscopic techniques such as ultraviolet visible spectroscopy (UV-Vis, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS).

22

Keywords: silver nanoparticles, characterization, morphology, operational factors

23 1. Introduction

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The field of nanotechnology is gaining more attention daily from different researchers based on the vast applications and its efficacy. Silver nanoparticle is a metallic nanoparticle with the size of 1–100 nm existing either as zerovalent silver (Ag⁰) or silver oxide due to their large ratio

01 of surface-to-bulk silver atoms. Of all the metallic nanoparticles, silver nanoparticles is excep-
02 tional and it is the most explored by researchers globally because of its various versatility,
03 simplicity of synthesis, adaptability, morphology and its extreme surface area that paves way
04 for the coordination of a vast number of ligands [1–9]. The following methods have been
05 identified for synthesis of silver nanoparticles: Wet chemistry, Ion implantation, Biological
06 synthesis and product functionalization. Wet chemistry involves nucleation of the
07 nanoparticles within the solution by the action of a reducing agent on the silver ion complex
08 forming colloidal silver. A number of wet chemistry methods, including the use of reducing
09 sugars, citrate reduction, reduction via sodium borohydride, the silver mirror reaction, the
10 polyol process seed-mediated growth and light-mediated growth have been identified [10–14].
11 However, reduction by borohydride is gradually facing out because of its toxicity thus the
12 major reason why biological method of synthesis has been more preferable. Biological method
13 of synthesizing silver nanoparticles may involve the use of bacteria, fungi and plant extract
14 using green synthesis route. This method is ecofriendly, low cost and silver nanoparticles
15 formed are stable and well dispersed with limited aggregation and good size control [15, 16].
16 There are different applications of silver nanoparticles ranging from its function as catalyst
17 [5, 17], water treatment [6], antimicrobial properties [8], chemotherapeutic agent and drug
18 delivery [18], Optical sensor [19], food packaging [20], and adsorption [21]. Although, there
19 have been reports on the synthetic routes and applications of silver nanoparticle, however,
20 nitty-gritty on the operational parameters imperative to the synthesis have not been so
21 reported and the cogent considerable factors in characterization have not been majorly
22 explored by researchers. Therefore, this book chapter aimed at taking a review survey of the
23 operational parameters (factors) and the characterization imperative to synthesis of silver
24 nanoparticles.

25 **2. Operational parameters for synthesis of silver nanoparticles**

26 The synthesis of silver nanoparticles depends on some important operational parameters.
27 Irrespective of the technique used for the synthesis of silver nanoparticles, certain operational
28 factors such as the concentration and volume ratio of reacting substances, reaction time,
29 temperature and pH influence the synthesis rate, size and shape of the nanoparticles. These
30 parameters could be varied to control its size, shape and general morphology, efficiency and
31 applicability. A survey of these operational parameters are examined in this section.

32 **2.1. Effects of concentration**

33 The silver ion concentration majorly affects the synthesis of silver nanoparticles. This parame-
34 ter was investigated to identify the amount of silver ion most suitable for the generation of
35 silver nanostructure. To investigate the effect of initial silver ion concentration, range of con-
36 centrations were prepared while other parameters was kept constant. The common practice is
37 to vary the concentration of Ag^+ ion from 10^{-3} to 10^{-2} M. Report from the literature have
38 established and approved 10^{-3} M as the most appropriate and suitable concentration where

01 better surface plasmon resonance was obtained. In most wet chemistry and biological synthetic
 02 methods, increase in silver ion intensity increases the rate at which the surface plasmon
 03 resonance will be attained. Silver nanoparticle is formed within the wavelength range of 400–
 04 490 nm with the formation of the ideal bell shape which is characteristic for the formation of
 05 Ag^0 nanoparticles [19].

06 Studies have shown that a variation in the concentration of metal salt used in the synthesis of
 07 nanoparticles influences the product of synthesis. Ibrahim [21] synthesized silver nanoparticle
 08 using silver nitrate as metallic salt and banana peel extract as reductant and capping agent,
 09 and reported a variation in color tending from yellowish brown to light reddish brown and
 10 darker shades of reddish brown with increasing silver nitrate concentration. Surface plasmon
 11 resonance (SPR) also attained distinctiveness with increasing concentrations of silver nitrate.
 12 These findings were also corroborated by reports from literature [22, 23]. Typical result of
 13 effect of concentration is shown in **Figure 1A**.

14 2.2. Effect of volume ratio

15 The volume ratio of silver ion solution to the extract which is serving as the reducing and
 16 stabilizing or sodium borohydride plays a substantive in the synthesis of silver nanoparticles.
 17 Report from different literature showed that in biological method/green synthesis route, excess
 18 silver ion is needed for better formation of the silver nanoparticles. In some instances, ratio 9:1
 19 (Silver ion solution: plant extract/broth) were used while in some other reports, ratio of 4:1 was

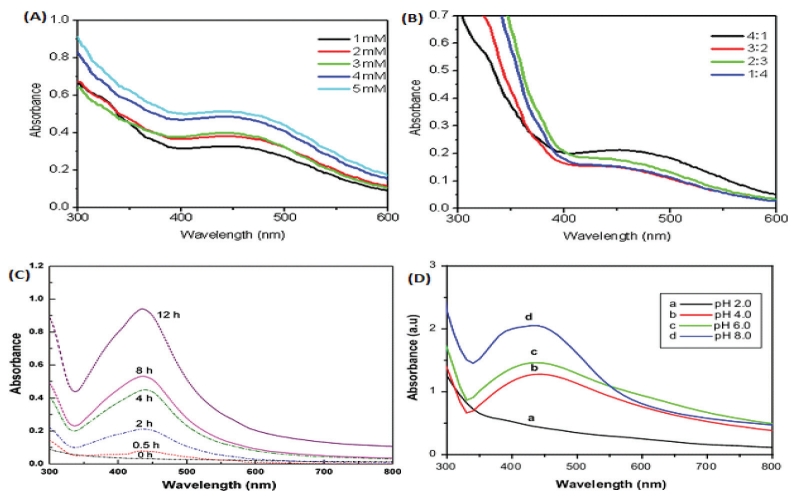


Figure 1. (A-D): (A) effect of variation of concentrations of Ag^+ solution (B) effect of volume ratio (C) effect of contact time (D) effect of change in pH carried out by different researchers [22–24].

01 used. Typical instances is seen in the synthesis of silver nanoparticle using *T. peruviana*
02 (Figure 1B). Omoloara et al., (2016) [23] investigated the influence of change in volume of
03 silver nitrate to *T. peruviana* aqueous leaf extract other parameters were kept constant. Different
04 volume ratios ranging from 4:1, 3:2, 2:3 and 1:4 of 1 mM silver nitrate to *T. peruviana*
05 aqueous leaf extract, respectively, were used. Excellent surface plasmon resonance (SPR) was
06 recorded on the UV-Vis at ratio 4:1. At 4 parts of 1 mM silver nitrate solution to 1 part of
07 *T. peruviana* aqueous leaf extract (4,1), the leaf extract bioreduced and stabilized the
08 nanoparticles with the plasmon resonance at 460 nm. Other volume ratios, 3:2, 2:3 and 1:4 of
09 1 mM silver nitrate to *T. peruviana* aqueous leaf extract did not give distinct characteristics SPR
10 for silver nanoparticles at the visible region of the UV-Vis. However, the in case of wet
11 chemistry method using sodium borohydride (NaBH_4) as the reducing agent, excess volume
12 of borohydride is needed for better formation of silver nanoparticle for better dispersion and
13 low agglomeration. Typical, the ratio of NaBH_4 to silver ion solution is 4:1 or 5:1 [25, 26].

14 2.3. Effect of contact time and temperature

15 Another important factor influencing the growth of silver nanoparticles is the contact time
16 which is also known as reaction time (Figure 1C). This was done by varying the time taken for
17 the formation of silver nanoparticle. Generally, the change in color to yellow or brown is an
18 evidence of the growth of silver nanoparticle. This is monitored with use of UV-Vis spectro-
19 photometer until the maximum absorption wavelength is reached with excellent surface
20 plasmon resonance (SPR). The intensity of the peak is function of the contact time therefore it
21 increases with increase in time. Contact time is one of the parameters that controls the size of
22 silver nanoparticles because of the blue shift of the adsorption peaks. It can be inferred that at
23 between 0 and 20 minutes (at the early stage), the SPR band is broadened because of the slow
24 conversion of silver ion (Ag^+) to zerovalent silver (Ag^0) nanoparticles. Increasing the contact
25 time enhances excellent plasmon band formation because large amount of Ag^+ has been
26 converted to Ag^0 . However, further increase in the contact time leads to noticeable decrease
27 in the absorption intensity and wavelength which is an indication of some aggregation of silver
28 nanoparticles leading to decrease in particle size [17, 19–23, 25, 26].

29 Temperature is another essential factor that should be considered in the synthesis of silver
30 nanoparticles because it controls the reaction kinetics of the synthetic process. Increase in
31 temperature is known to increase the rate of reaction because there will be an increase in the
32 effective collision and the frequency factor of the reacting species. From the literature reports,
33 studies showed that increase in temperature leads to increase in the intensity of the plasmon
34 band as a result of bathochromic shift resulting in a decrease in the mean diameter of silver
35 nanoparticle. At the beginning of the reaction, the synthesis of AgNPs may be rapid but this
36 does not connote optimum temperature of the system because low temperature readily under-
37 scores the ability of reducing and stabilizing agent [27, 28].

38 2.4. Effect of pH

39 There are so many factors that influence the reduction of silver ion to AgNP. Effect of pH as
40 one of the operational parameters plays a major role because it influences the chemistry of the

01 silver nanoparticle synthesis (**Figure 1D**). This is carried out by pH adjustment using phos-
02 phoric acid or hydrochloric acid and sodium hydroxide. In practice, during green synthesis,
03 the extract pH is adjusted from pH 2 to 11 and its reduction process monitored by UV-Vis
04 spectrophotometer. This change in the chemical nature of the extract affects its performance as
05 well as the rate of reduction. In the study carried out by Heydari and Rashidipour on the green
06 synthesis of silver nanoparticles using extract of Oak fruit hull, the result showed that the rate
07 of AgNPs synthesis increases with increasing pH up to pH = 9 and then decrease [29]. More so,
08 investigation carried out by Kokila et al., on biosynthesis of silver nanoparticles from Caven-
09 dish banana peel extract and its antibacterial and free radical scavenging assay showed that
10 formation of AgNPs depends mostly on the pH of the reaction medium. The result confirmed
11 that formation of silver nanoparticles is favorable in the basic medium than in acidic medium
12 because the absorbance values increase with increase in pH. This could be accredited to the
13 ionization of the functional groups at higher pH and the slow rate of reduction observed in the
14 acidic medium could be attributed to electrostatic repulsion of anions present in the reaction
15 mixture. This was in accordance with the findings in the literature [30–34].

16 3. Characterization

17 One of the main problems confronting scientists is understanding the properties a novel
18 material displayed. This can only be achieved by knowing and determining the structure of
19 this new material by characterization. Presently, there is an established and well accepted
20 concept that structures are driven by properties. This is acknowledged in chemistry and in all
21 fields where chemistry plays a primary character such as biochemistry, biology, environmental
22 science, engineering, medicine, polymer science and nutrition. The make-up or property of a
23 nano/biomaterial is placed into three groups i.e. chemical (e.g., equilibrium position, reaction
24 rates, etc.), physical (e.g., melting/boiling points, solubility, spectra, symmetry, etc.) and bio-
25 logical (e.g., color, drug action, odor, taste, toxicity, etc.). This property gives rise to structural
26 features which affect intensely the macroscopic character of the material. Since this is a struc-
27 ture driven properties concept, the structure of the novel material mostly signifies its compo-
28 sition at each level of complexity. However, this varies from the simple molecule formula
29 (giving the ratio that the elements present bears to each other) and the exact positions and
30 locations of all atoms in the molecules of this novel material referring to the three (3) dimen-
31 sional electronic density distribution [35]. This section of book chapter therefore, excellently
32 and succinctly state the relevance of various characterization techniques relevance to the
33 synthesis of silver nanoparticles.

34 3.1. UV: Vis spectroscopy

35 Ultraviolet visible spectroscopy (UV-Vis Spec) remains the most useful characterization rele-
36 vant to the synthesis of silver nanoparticles [2–23, 25–28]. In principle, the absorption of light
37 occurs in the visible region of the electromagnetic spectrum where atoms and molecules
38 undergo electronic transition of $\pi\text{-}\pi^*$, $n\text{-}\pi^*$, $\sigma\text{-}\sigma^*$, and $n\text{-}\sigma^*$. Absorption of energy in the form

01 of ultraviolet or visible light is by molecules containing π -electrons or non-bonding electrons
02 (n-electrons) to excite these electrons to higher anti-bonding molecular orbitals. The length of
03 wave depends on the excitation of the electrons. The more easily excited the electrons the
04 longer the wavelength of light it can absorb. The absorption in the visible range directly affects
05 the perceived color of the chemicals involved. UV-Vis in silver nanoparticle synthesis provides
06 vivid information on the surface plasmon resonance (SPR) at the absorption maximum wave-
07 length. The surface plasmon resonance comes from the free electron arising from the conduc-
08 tion and valence bands lying close to each other in metal nanoparticles. It is as a result of the
09 collective oscillation of free electron of silver nanoparticles in resonance with the light wave in
10 silver nanoparticle synthesis [36, 37]. All the experimental operational parameters vis-à-vis
11 effect of initial concentration, contact time, temperature, pH, and volume ratio are monitored
12 using the UV-Vis spectrophotometric technique. Information obtained from the absorption
13 spectrum as a result of SPR surface, gives a clue on the type of shape of the silver nanoparticles.
14 It is important that the interpretation from the UV-Vis measurement corroborates with TEM
15 measurement [38]. **Figure 1(A-D)** portray different UV-Vis spectra at various operational
16 factors influencing the synthesis in the studies carried by researchers.

17 3.2. Fourier transform infrared spectroscopy (FTIR)

18 The nature, structure and physicochemical properties of silver nanoparticles (AgNPs) are
19 imperative to their activity, behavior, bio-distribution and safety. Therefore, characterization
20 of AgNPs is essential and important for the assessment of the functional features and charac-
21 teristics of the synthesized nanoparticles.

22 FTIR measurements is usually carried out to identify the possible biomolecules which are
23 involved in the synthesis of nanoparticles and to find out their functions in reduction and
24 stabilizing the nanoparticles. This spectroscopy method is employ to detect and distinguish
25 small absorption bands (changes on the order of 10^{-3}) of functional group covalently grafted
26 onto silver or functionally active points that is characteristics to AgNPs. This method has the
27 ability to give precision, it is easily reproducible and also a favorable signal-to-noise ratio [39-
28 41]. One of the major advantage of FTIR spectrometers to other methods of characterization of
29 AgNPs is that, it is a non-invasive technique, data are collected rapidly data, signals are strong
30 and bold, large signal-to-noise ratio, and very little sample is heat-up [42].

31 Lately, attenuated total reflection (ATR)-FTIR spectroscopy which is more advance in mea-
32 surement than the conventional FTIR method has been discovered [43]. Using ATR-FTIR, we
33 can easily know and establish the chemical properties on the polymer surface, nanoparticle
34 surfaces and nature, its sample preparation is very simple when compared to conventional
35 FTIR [44]. Therefore, FTIR as a method is appropriate, indispensable, non-invasive, affordable,
36 easy and hands-on technique to know the function of biological molecules in the reduction of
37 silver nitrate to silver.

38 Identification of the functional groups or biomolecules which are responsible for the reduction
39 of silver ions in silver nanoparticles could be achieved by the Fourier transform infrared (FTIR)
40 spectroscopy. This is achieved by comparing the intense bands with standard values. The

01 proportionate shift in band revealed after treatment with silver nitrate is a likely indication of
02 participation of the functional groups in the process of nanoparticle synthesis [45].

03 3.3. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

04 The significance attributes of synthesized silver nanoparticles have been documented to have a
05 greater consequence on their behavior and toxicity encompasses of particle size, shape, surface
06 properties, aggregation state, solubility, structure and chemical make-up. The characterization
07 of silver nanoparticle is necessary for proper insight into the formation, synthesis and their
08 utilization in various fields including agriculture, medical, industries, and environment [46,
09 47]. The validation and confirmation of synthesized nanoparticle have been carried out using
10 various techniques however transmission electron microscopy (TEM) and scanning electron
11 microscopy (SEM) is important methods for the cases. The significant of Microscopic techni-
12 ques in the characterization of silver nanoparticles cannot be overemphasized because they
13 give a more clear insight from the obtained data on the size, size distribution, and other
14 quantifiable properties. The significant of electron microscopy in the analysis the synthesized
15 silver premised on their ability to show the real structure of the particle between some ranges
16 of nanometers (nm) conventional bright field images and the intermediate resolution darkfield
17 techniques, to the high-resolution atomic images [48].

18 3.3.1. Scanning electron microscopy (SEM)

19 The SEM works by producing images whenever the electron beams scanning probe the periph-
20 eral surface of the given sample in order to confirm its structure as well as the topographical and
21 elemental composition present in the materials [48]. During SEM analysis the electrons possess
22 large amount of kinetic energy that is distributed and eventually leads to the generation numer-
23 ous signals during the analysis of samples during whenever they interacts with the surface of the
24 atom in the sample. The generated signal are secondary electrons, backscattered electrons,
25 characteristics X rays, cathodoluminescence, specimen current and transmitted electrons which
26 can generate a high-resolution magnified descriptions of a synthesized silver nanoparticle, illu-
27 minating facts with sizes that varies from 1 to 5 nm in size. Appropriate signals are collected
28 depending upon the mode of operation of the instrument. The numerous field observed in SEM
29 could be linked to the facts that it produced a large depth of field. Many researchers have utilized
30 SEM for the determination of various synthesized silver nanoparticles including, polyhedral [49],
31 flake flower [50], hexagonal [51], isotropic [52], irregular [53], triangular [54], anisotropic [55] and
32 rod like structures [56], pentagonal [57].

33 3.3.2. Transmission electron microscopy (TEM)

34 The TEM works based on the application of a very high resolution microscopy method to
35 generate an image as well as a diffraction patterns of the atomic size as well as shape of
36 material by focusing the electron beam that can penetrate through the given material as well
37 as interact with the sample of microstructure of materials. The major difference between TEM
38 and SEM is that it can detect the following in the synthesized silver nanoparticles in a micro-
39 structure, crystallographic defects, line defects and planar defects. Another major difference is

01 that TEM could determine the available elemental composition at nano level [58, 59]. There are
02 different forms of TEM including high-resolution transmission electron microscopy (HRTEM),
03 scanning transmission electron microscopy (STEM) and analytical transmission electron
04 microscopy (ATEM). TEM also shows a better image, diffraction properties, and the chemical
05 analysis competences when compared to SEM. TEM can also detect a small size up to 0.2 nm
06 when compared to SEM. Also, TEM produced a better resolution image because it utilized a
07 low wavelength electron when compared to SEM. Finally, TEM can shift from diffraction to
08 imaging by shifting the excitation of the lenses following the objective lens. TEM can be
09 utilized to capture silver synthesized particle image in the plane of the fluorescent screen as
10 well as the diffraction pattern from the particles. The nanoparticle size and particle size
11 distribution of the synthesized nanoparticle could be determined and evaluated by transmis-
12 sion electron microscopy (TEM) and high-resolution microscopy. Moreover, the application of
13 image J software for the plotting of histogram by measuring the size of different nanoparticles
14 could be explored. Some of the demerits of using TEM entails required high vacuum, thin
15 sample section, time consuming for the sample preparation [60]. Further insight and details
16 about the morphology of AgNPs are provided by TEM. The most common size of the silver
17 nanoparticles from various TEM image is spherical [61].

18 3.4. Energy-dispersive X-ray spectroscopy (EDX) and X-ray fluorescence (XRF)

19 The elemental constituents and composition of nano-materials could be determined by EDX
20 and XRF. This section explores the principle and relevance of these analytical techniques in
21 nano-research and most especially, silver nanoparticles studies.

22 3.4.1. Energy-dispersive X-ray spectroscopy (EDX)

23 Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique that gives information
24 on the surface atomic distribution and the chemical elemental composition [62–65]. In most
25 cases, the EDX is always coupled with SEM. The EDX is used in the elemental determination of
26 composition of the silver nanoparticles.

27 In Practice, it relies on an interaction of some source of X-ray excitation and a sample. Its
28 characterization capabilities are due in large part to the fundamental principle that each
29 element has a unique atomic structure allowing a unique set of peaks on its electromagnetic
30 emission spectrum. In order to determine the peak of an element, a high energy beam of
31 electron or beam of X-ray is targeted toward the sample to analyze. Excitation of electrons in
32 the inner shell (lower energy level) occurs via the incident beam creating an electron holes
33 which electron from the outer shell (higher energy level) fills. The difference between the
34 higher and lower energy levels is released in form of an X-ray. The number and energy of the
35 X-rays emitted from the silver nanoparticle can be measured by an energy-dispersive spec-
36 trometer. Electron beam excitation is used in electron microscopes, scanning electron micro-
37 scopes (SEM) and scanning transmission electron microscopes (STEM). X-ray beam excitation
38 is used in X-ray fluorescence (XRF) spectrometers. A detector is used to convert X-ray energy
39 into voltage signals; this information is sent to a pulse processor, which measures the signals
40 and passes them onto an analyzer for data display and analysis [66, 67]. Most researchers

01 utilize EDX for characterization of silver nanoparticles than XRF. Report from the literature
02 vividly revealed that AgNPs signal is detected at 3.0 keV [19, 22, 23, 61, 68–70].

03 3.4.2. X-ray fluorescence (XRF)

04 This is the emission of characteristic “secondary” (or fluorescent) X-rays from a material that
05 has been excited by bombarding with high energy x-rays or gamma rays. XRF technology
06 provides one of the simplest, most accurate and most economic analytical methods for the
07 determination of the chemical composition of many types of materials, particularly in the
08 investigation of metals, glass, ceramics and building materials, and for research in geochemis-
09 try, forensic science and archeology. It is non-destructive and reliable, requires no, or very little,
10 sample preparation and is suitable for solid, liquid and powdered samples. It can be used for
11 wide range of elements and provide detection limits at the sub-ppm level; it can also measure
12 concentrations of up to 100% easily and simultaneously [71].

13 In principle, an inner shell electron is excited by an incident photon in the X-ray region. During the
14 de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy
15 difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum
16 acquired during the above process reveals a number of characteristic peaks. The energy of the peaks
17 leads to the identification of the elements present in the sample (qualitative analysis), while the peak
18 intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative
19 analysis) [72]. A typical XRF spectroscopy arrangement includes a source of primary radiation
20 (usually a radioisotope or an X-ray tube) and equipment for detecting the secondary X-rays. When
21 materials are exposed to short wavelength x-rays or to gamma rays, ionization of their component
22 atoms may take place. If an X-ray beam is used to excite atoms in a sample, electrons near the
23 nucleus emit secondary fluorescent x-rays on reversion to their original states [73].

24 In silver nanoparticle studies, XRF could be employed for elemental determination of the
25 composition of nanoparticles although this is not frequently used compared to EDX. The X-
26 ray fluorescence technique is of special interest for the analysis of silver nanoparticles because
27 the technique is not only fast, sensitive and capable of simultaneous multi-element analysis,
28 but also ensures that the sample can be quantitatively analyzed without damage. Therefore, it
29 is mostly used to identify determining the presence of silver and other element in the com-
30 pound. Specifically, silver nanoparticle is detected at 3.0 keV which is the characteristic peak
31 reported by different researchers [74].

32 3.5. X-ray diffraction (XRD)

33 X-ray diffraction (XRD) (among others, such as FT-IR, UV, TEM, SEM, EDX) is a widely used
34 technique for structural characterization which participate (a main part) in identifying the
35 structure of a (nano/bio)-material or particle. Hence, XRD is a widely held analytical technique,
36 which has been employed in the analysis of both molecular and crystal structures, qualitative
37 detection of elements and their compounds, quantitative resolution of chemical species, quan-
38 tifying the degree/measure of crystallinity, isomorphous substitutions, stacking faults, poly-
39 morphisms, particle sizes, *in situ* studies at process temperatures and in reactive atmospheres,
40 phase identification and quantification etc. [75, 76].

01 XRD technique is a handy popular technique for characterizing silver nanoparticles and has
02 grown into a common characterization method for evaluating these nanoparticles. Some of the
03 main structural uniquenesses are related with these i.e., measuring degree of crystallinity, phase
04 identification, super-lattice generation, impurities detection, material's vacancy characteriza-
05 tion and also novel materials development [77]. The crystalline structure or nature of bio-
06 synthesized silver nanoparticles is determined by XRD analysis and patterns; this also use to
07 confirm the structural information. Many authors reported a similar diffraction profile for
08 most Ag-NPs with XRD peaks at 2θ of 38.18° , 44.25° , 64.72° , and 77.40° which are indexed to
09 the 111, 200, 220, and 311 crystallographic planes of Bragg's reflections of the face-centered
10 cubic structure of silver crystals, which suitably matched the standard diffraction data with
11 those reported for silver by joint committee on powder diffraction standards. The average
12 crystalline size of the silver nanoparticles was estimated using (Eq. 1), the Debye-Scherrer's
13 equation [45, 78]:

$$D = 0.9\lambda / \beta \cos \theta \quad (1)$$

14 where d is the particle size, λ is the wavelength of X-ray radiation (1.5406 \AA), β is the full-width
15 at half-maximum (FWHM) of the height (in radians) and 2θ is the Bragg angle. The precision,
16 significance, sensitivity and easy use of XRD increases its importance in AgNPs. However,
17 there are some limitations that one might face using this analysis. It can only analyze and
18 identify an unknown material that is homogeneous and single phase. There should be a
19 standard reference file for compounds especially inorganic ones (d -spacings, hkl s), peaks
20 overlay mostly happened in XRD and worsen for high angle' reflections, to determine unit cell
21 using XRD, indexing of patterns for non-isometric crystal systems is complicated.

22 3.6. Thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS)

23 The advancement of nanotechnology is rapidly evolving and holds potential to completely
24 redefine applications of material science in the nearest future. In order to maximize the
25 prospects of nanotechnology for diverse applications, the characterization of nanomaterials
26 and/or nanoparticles have become imperative. Among the several techniques available for the
27 characterization of nanomaterials are thermogravimetric analysis (TGA) and X-ray photoelec-
28 tron spectroscopy (XPS).

29 3.6.1. Thermogravimetric analysis

30 Thermogravimetric analysis (TGA) is an analytical technique for measuring changes in the
31 mass of a material that occur in response to programmed temperature changes [79]. TGA
32 represents a branch of thermal analysis examining the mass changes of a sample as a function
33 off temperature (in the scanning mode) or as a function of time (in the isothermal mode). In
34 TGA changes in physical and chemical properties of materials are measured as a function of
35 increasing temperature (with constant heating rate), or as a function of time (with constant
36 temperature and/or constant mass loss). The changes in the mass of a sample due to various
37 thermal events (desorption, absorption, sublimation, vaporization, oxidation, reduction and
38 decomposition) can be studied while the sample is subjected to a program of change in
39 temperature. TGA has found applications in the analysis of volatile products, gaseous

01 products lost during the reaction in thermoplastics, thermosets, elastomers, composites, films,
02 fibers, coatings, paints among others. Further practical applications, are determining composi-
03 tion and thermal stability of materials, evaluating the kinetics of thermally stimulated pro-
04 cesses, predicting lifetimes, and studying reactions of materials with gases. There are different
05 types of TGA ranging from isothermal to dynamic TGA.

06 3.6.1.1. *Thermal properties of silver nanoparticles*

07 In a recent investigation, thermal behavior of silver nanoparticles was monitored by TGA
08 Khan et al. [80], authors reported dominant weight loss in silver nanoparticles occurred in
09 temperature region between 200 and 300°C. There was almost no weight loss below 200°C and
10 above 300°C. The weight loss was attributed to the evaporation of water and organic compo-
11 nents. Overall, TGA results show a loss of 14.58% up to 300°C. In the same study, the differen-
12 tial thermal analysis (DTA) plot displayed an intense exothermic peak between 200 and 300°C
13 which mainly could be attributed to crystallization of silver nanoparticles. DTA profiles sug-
14 gest that complete thermal decomposition and crystallization of the sample occur simulta-
15 neously. Taken together, the TGA/DTA study shows that the dominant weight loss occurs
16 between 200 and 300°C; and the reaction is of exothermic type [80].

17 In a separate study, the low-temperature sintering behavior of Ag nanoparticles was investi-
18 gated. The silver nanoparticles were shown to exhibit obvious sintering behavior at significantly
19 lower temperatures (~150°C) than the T_m (960°C) of silver while coalescence of the silver
20 nanoparticles was observed by sintering the particles at 150, 200, and 250°C. The thermal profile
21 of the nanoparticles was examined by a differential scanning calorimeter (DSC) and a thermogra-
22 vimetric analyzer (TGA). Shrinkage of the silver nanoparticle compacts during the sintering
23 process was observed by thermomechanical analysis (TMA). Sintering of the nanoparticle pellet
24 led to a significant increase in density and electrical conductivity. The size of the sintered particles
25 and the crystallite size of the particles increased with increasing sintering temperature [81].

26 3.6.2. *X-ray photoelectron spectroscopy (XPS)*

27 As the demand for high performance materials increases, so does the importance of surface
28 engineering. Typically, the surface of a material represents the platform of interaction with the
29 external environment and other materials. In the case of nanotechnology, surface chemistry of
30 nanomaterials and/or nanoparticles is key to exploring the prospects of these particles for
31 diverse applications. Surface modification can be used to alter or improve the properties of
32 nanomaterials and/or nanoparticles, and so surface analysis becomes a technique for probing
33 the surface chemistry of these particles. More so, nanotechnology approaches include surface
34 modification of nanomaterials in order to suit specific purposes. Therefore, it becomes expedi-
35 ent to understand the physical and chemical interactions occurring at the surface, or at the
36 interfaces of the nanomaterial's layers.

37 X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical
38 analysis (ESCA) is a widely accepted technique for surface analysis. This probably may be
39 because XPS can be applied to a broad range of materials and provides valuable quantitative
40 and chemical state information from the surface of the material being studied. The average
41 depth of analysis for an XPS measurement is approximately 5 nm. XPS measurement involves

01 irradiating the surface of sample materials with monochromatic Al-K- α x-rays. This leads to
02 excitation thereby causing photoelectrons to be emitted from the sample surface. Then an
03 electron energy analyzer is used to measure the energy of the emitted photoelectrons. From
04 the binding energy and intensity of a photoelectron peak, the elemental identity, chemical
05 state, and quantity of a detected element can be determined.

06 3.6.2.1. X-ray photoelectron spectroscopy (XPS) of silver nanoparticles

07 Several investigations have reported the use XPS technique to characterize the surface chemis-
08 try of silver nanoparticles. Larrude et al. [82] characterized silver-multiwalled carbon
09 nanotubes (Ag-MWCNTs) nanocomposite using the XPS technique. Their report showed spec-
10 trum revealing the dominance of silver and carbon, with small amounts of sodium and sulfur
11 in the sample. According to the author of the investigation, presence of Na and S was attribut-
12 able to the use of sodium dodecyl sulfate (SDS) for the MWCNTs dispersion. Also, the study
13 demonstrated increased oxygen content compared to a pure MWCNTs sample. However,
14 there was no evident relationship between the oxygen and the silver contents because the O/
15 Carbon atomic rate did not change significantly between the different silver concentrations.
16 Furthermore, the spectrum of the Ag 3d core level of the Ag-decorated MWCNTs, confirmed
17 the presence of metallic silver because the 3d_{5/2} component occurred at a binding energy of
18 368.3 eV, which is characteristic of the metallic Ag (0) oxidation state [82].

19 In a separate study involving a surface chemical characterization of silver nanoparticles thin
20 film using XPS instrument equipped with monochromatic Al-K- α X-ray source [83]; the XPS
21 spectrum and the high-resolution XPS window of the core level atoms comprising the silver
22 nanoparticles capped with carboxylate/1-dodecylamine revealed the presence of Ag, C, O, and
23 N atoms according to their binding energies. The most prominent signal in the XPS spectrum
24 was the Ag 3s consisting of two spin-orbit components at 368.8 (Ag3d_{5/2}) and 374.8 (Ag3d_{3/2})
25 eV and separated by 6.0 eV. Moreover, the deconvolution of Ag (3d) doublet revealed asym-
26 metric peak shape. These two characteristics indicated the existence of the Ag in metallic form.

27 Furthermore, another investigation reported consistence of the XPS analysis of silver behenate
28 was with the theoretical C: O: Ag atomic composition. The report noted that brown discolor-
29 ation of silver behenate powder within a few seconds of exposure to monochromatic X-rays
30 and that this increased significantly with time. Further, noticeable changes to the XPS spectra
31 and the observed surface composition begin to occur after about 30 minutes of X-ray exposure,
32 while prolonged exposure to monochromatic X-rays resulted in significant changes in the C 1s,
33 O 1s, and Ag 3d peak shapes and positions. Changes in the XPS spectra indicated that
34 exposure to Al K α X-rays resulted in the formation of silver metal particles and decomposition
35 of the carboxylic acid portion of the molecule to hydrocarbon species. Thermal reduction of
36 silver behenate powder produced similar changes in the XPS spectra [84].

37 4. Conclusion

38 This chapter has examine the operational parameters which are imperative to the synthesis of
39 silver nanoparticles. Effect of concentration, volume ratio, contact time, temperature and pH

01 affect the synthesis of silver nanoparticles. Conditions attached to each of these have been
02 identified. Chief among these factors is the effect of pH which affect the chemistry of the silver
03 nanoparticle synthesis. However, irrespective of the synthetic route and conditions, character-
04 ization techniques germane to the studies of silver nanoparticles have also the critically exam-
05 ined. The UV-Vis spectroscopy helps in determining the surface plasmon resonance
06 absorption band and this is major in nanoparticle studies. The functional groups are deter-
07 mined by FTIR, morphology and sizes by SEM and TEM, atomic distributions and relative
08 abundances were revealed by EDX and XRF respectively. The crystallinity determined by
09 XRD, surface chemical characterization by X-ray photoelectron spectroscopy (XPS) and silver
10 content by thermogravimetric analysis (TGA). It can be concluded that relevant research in
11 nanoparticle studies rely on both the operational conditions and excellent characterization.

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15 **Conflict of interest**

16 The authors declare that there is no conflict of interest.

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