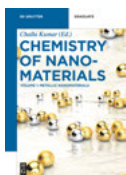
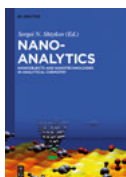


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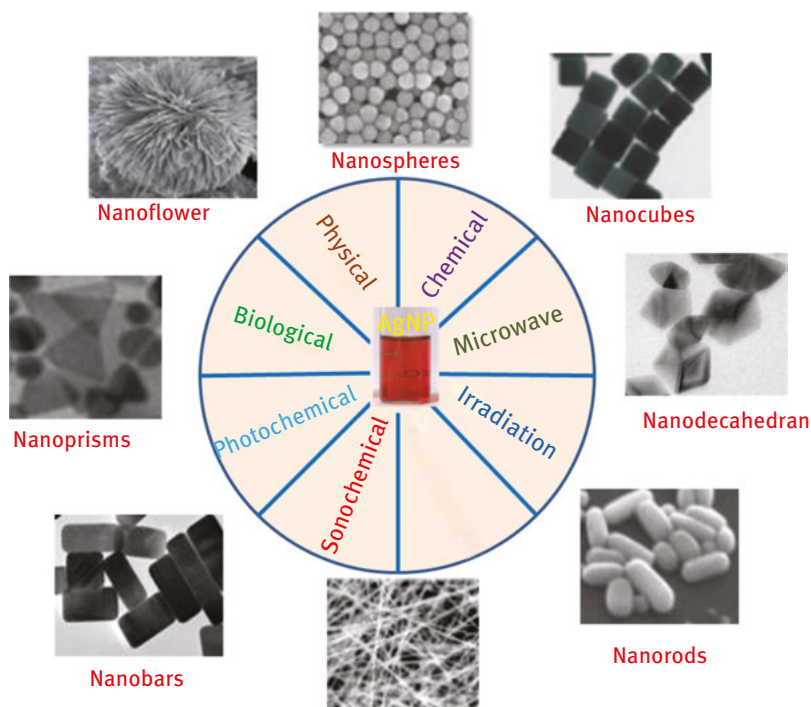
Suparna Mukherji, Sharda Bharti, Gauri Shukla
and Soumyo Mukherji

1 Synthesis and characterization of size- and shape-controlled silver nanoparticles

Abstract: Silver nanoparticles (AgNPs) have application potential in diverse areas ranging from wound healing to catalysis and sensing. The possibility for optimizing the physical, chemical and optical properties for an application by tailoring the shape and size of silver nanoparticles has motivated much research on methods for synthesis of size- and shape-controlled AgNPs. The shape and size of AgNPs are reported to vary depending on choice of the Ag precursor salt, reducing agent, stabilizing agent and on the synthesis technique used. This chapter provides a detailed review on various synthesis approaches that may be used for synthesis of AgNPs of desired size and shape. Silver nanoparticles may be synthesized using diverse routes, including, physical, chemical, photochemical, biological and microwave -based techniques. Synthesis of AgNPs of diverse shapes, such as, nanospheres, nanorods, nanobars, nanoprisms, decahedral nanoparticles and triangular bipyramids is also discussed for chemical-, photochemical- and microwave-based synthesis routes. The choice of chemicals used for reduction and stabilization of nanoparticles is found to influence their shape and size significantly. A discussion on the mechanism of synthesis of AgNPs through nucleation and growth processes is discussed for AgNPs of varying shape and sizes so as to provide an insight on the various synthesis routes. Techniques, such as, electron microscopy, spectroscopy, and crystallography that can be used for characterizing the AgNPs formed in terms of their shape, sizes, crystal structure and chemical composition are also discussed in this chapter.

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Graphical Abstract:

Keywords: silver nanoparticles, synthesis routes, nanospheres, nanoplates, nanoprisms, nanorods

1.1 Introduction

Nanoparticles (NPs) can be defined as small structures where one of the dimensions is of nanometre size range, i. e. 1–100 nm. NPs inherently possess a high surface area to volume ratio, which imparts higher reactivity to the NPs as compared to their bulk metallic form. The localized surface plasmon resonance (LSPR) frequency varies with the morphology of the NPs and the dielectric nature of the surrounding environment. The size and shape of NPs impart unique physical, electronic, catalytic and optical properties and determine their potential application [1–4]. Decrease in the metal core size changes the energy-level structure such that the continuous band of energy levels change to discrete energy levels, resulting in strong size-dependent physical and chemical properties. Among all metallic NPs studied, silver NPs (AgNPs) have been studied most widely. Aspects such as, synthesis routes, optical properties and

catalytic properties and their use in various applications have been extensively explored. The physical, chemical, catalytic, optical, magnetic and electronic properties vary with the size and shape of the NPs, their interactions with stabilizers and the surrounding media and the synthesis method employed. The application areas for AgNPs include chemical sensing, biological sensing, pollutant removal through catalysis and antimicrobial applications [5–7]. Numerous researchers have focussed on size- and shape-controlled synthesis of AgNPs for various applications.

A number of excellent reviews are available on synthesis and application of AgNPs. They have focused on diverse synthesis routes [8–11], application in various domains [2, 12–14] and synthesis of AgNPs of diverse shape [15]. Most of the reviews have focused on a particular domain with respect to the synthesis of AgNPs, such as, shape-controlled synthesis of AgNPs [16, 17], physical synthesis approaches [18], microbial synthesis [9, 19–21], bacteria-mediated synthesis [10, 22], plant-mediated synthesis [23], green synthesis [8, 24] or microwave -based synthesis [25], while some others have selectively reviewed a few of the synthesis routes for production of shape-controlled AgNPs [3, 11, 13, 15, 26–28]. None of the reviews available on silver NP synthesis have comprehensively discussed all the synthesis approaches in depth. This chapter discusses the synthesis approaches starting from the synthesis of spherical AgNPs to synthesis of shape-controlled AgNPs and also discusses how size-controlled AgNPs can be synthesized. A preview of the characterization techniques presented before discussion on synthesis allows better comprehension of the characteristics of the AgNPs synthesized using each process. An attempt is made to provide insight on the mechanisms involved in the various synthesis processes. This allows a more scholarly discourse on the various synthesis routes and mechanisms, and elucidates how shape- and size-controlled synthesis of silver NPs can be achieved through appropriate choice of energy source, chemicals used as precursor, reducing agent and capping agent as well as the selection of concentration and molar ratio of the chemicals. Figures and tables are used to illustrate the diverse synthesis options available for synthesizing AgNPs of the desired size and shape. Finally, safety considerations are also discussed in this review since not only does synthesis involve numerous hazardous chemicals, adequate precaution is needed to prevent inadvertent release of the AgNPs thus synthesized. The overall breadth and detailed coverage will enable scientists, who are not completely familiar with the domain, to understand and appreciate the various techniques that have evolved over decades of international research.

1.2 Characterization of silver NPs

To establish the success of any NP synthesis protocol, it is important to characterize the NPs synthesized in terms of shape, particle size distribution, solubility, morphology, surface area, crystallinity, pore size, dispersivity in solution, and

aggregation behaviour. The commonly used characterization techniques include UV-Vis spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Fourier Transform Infra-Red (FTIR) spectroscopy, dynamic light scattering (DLS) and zetasizer. The shape and size distribution of AgNPs is typically measured and visualized using electron microscopy techniques, such as, TEM and SEM. The SPR band or absorption spectra can be obtained using UV-Visible spectroscopy, where the wavelength corresponding to peak absorbance (λ_{max}) reflects the size of the AgNPs. For AgNPs, the peak is usually in the range of 400–450 nm [29]. These and other techniques that can provide further insights on the silver NPs synthesized are discussed in the following section.

1.2.1 UV-Vis spectroscopy

The UV-visible optical absorption spectrum and the λ_{max} value of metallic NPs depend on the type of metal, on the size and shape of the NPs and on the dielectric media it is dispersed in. It is an outcome of the LSPR phenomena caused by collective oscillation of electrons in specific vibrational modes in the conduction band near the particle surface in response to light. The UV-Vis spectrum is also affected by the free electron density and inter-particle interactions. This same phenomenon is responsible for the intense colour that characterizes a dispersion of colloidal AgNPs due to scattering and absorption of visible light. The latter is affected by the energy of the photons which can induce conduction electrons to oscillate by absorbing incident electromagnetic radiation. Apart from characterization of the AgNPs, this technique is commonly used to study the stability/aggregation tendency of AgNPs over time [30]. In unstable colloidal dispersions, the plasmon resonance peak shifts to longer wavelengths and broadens as the diameter increases due to aggregation [29]. Thus, aggregated NPs would exhibit red-shifted LSPR peak with respect to the peak of well-dispersed freshly synthesized NPs. The aggregation state of the NPs may also be revealed through determination of effective size of the NPs in solution through alternative techniques, such as, DLS. Silver NPs exhibit unique extinction peak corresponding to their size. Agnihotri et al. [29] reported SPR peaks in UV-Vis spectra at wavelength 393, 394, 398, 401, 406, 411, 420, 429, 449, and 462 nm corresponding to AgNPs of average size 5, 7, 10, 15, 20, 30, 50, 63, 85, and 100 nm, respectively (Figure 1.1a). Moreover, distinct colour was observed with change in size of the AgNP colloidal suspensions, as shown in Figure 1.1b.

The absorbance spectra of AgNPs is also reported to reflect alteration in shape of AgNPs. Such changes in UV-Vis-NIR spectra were illustrated during photochemical synthesis of Ag nanoprisms grown by illuminating small silver NP seeds (λ_{max} of 397 nm) with low-intensity light-emitting diodes (LEDs) [31]. As the seeds were converted to nanoprisms, the peak absorbance at 397 nm decreased over time and new

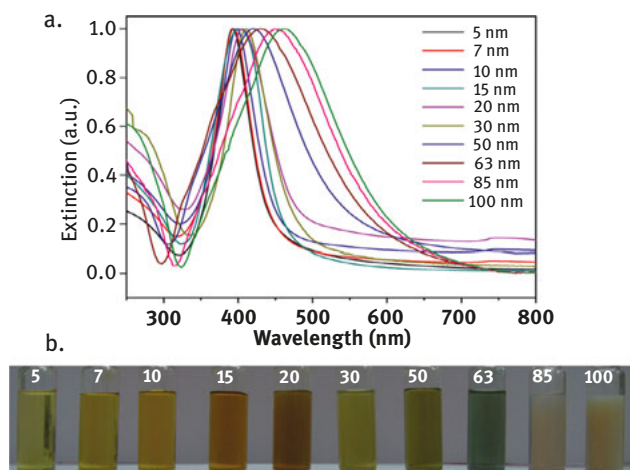


Figure 1.1: Variation in (a) UV-Vis absorption spectra and (b) distinctive colour of colloidal AgNP suspension of varying size (Reprinted from ref. [29], Published by The Royal Society of Chemistry).

peaks appeared at 1330 nm and 890 nm representing the LSPR of the nanoprisms formed. An intermediate stage of aggregated NPs was reflected by a red shift in the peak at 397 nm before the peaks due to nanoprisms appeared. Thus, UV-Vis-NIR spectra can reveal insights on the shape and size of NPs.

1.2.2 Transmission electron microscopy

High-resolution imaging of NPs below the wavelength of visible light is possible due to the fact that de Broglie wavelength of electrons is orders of magnitude lower compared to photons. Thus, if a beam of electrons is incident on NPs, fine details on shape, size and crystal structure of NPs is revealed in the transmission image that is formed. This technique is known as TEM. Further analysis of the image through image analysis software can provide information on uniformity in terms of shape and size, size distribution and aspect ratio thereby indicating success of a synthesis protocol in generating NPs of controlled size and shape. Imaging at various stages during the synthesis can illustrate the emergence of NPs of distinct shape as illustrated in Figure 1.2.

Figure 1.2a shows small quasi-spherical AgNP seeds and multiply twinned particles (MTPs) ~20 nm in size. Over 16 h, the seed and MTPs formed decahedral NPs with progressive increase in edge length. The edges were found to be irregularly etched (Figure 1.2f, Figure 1.2g) and were characterized by saw-toothed structures [32].

In addition to imaging, TEM can also be used for detection of diffraction ring pattern corresponding to a specific lattice plane/crystal structure. Selected area electron diffraction (SAED) pattern is generated due to scattering of electrons by

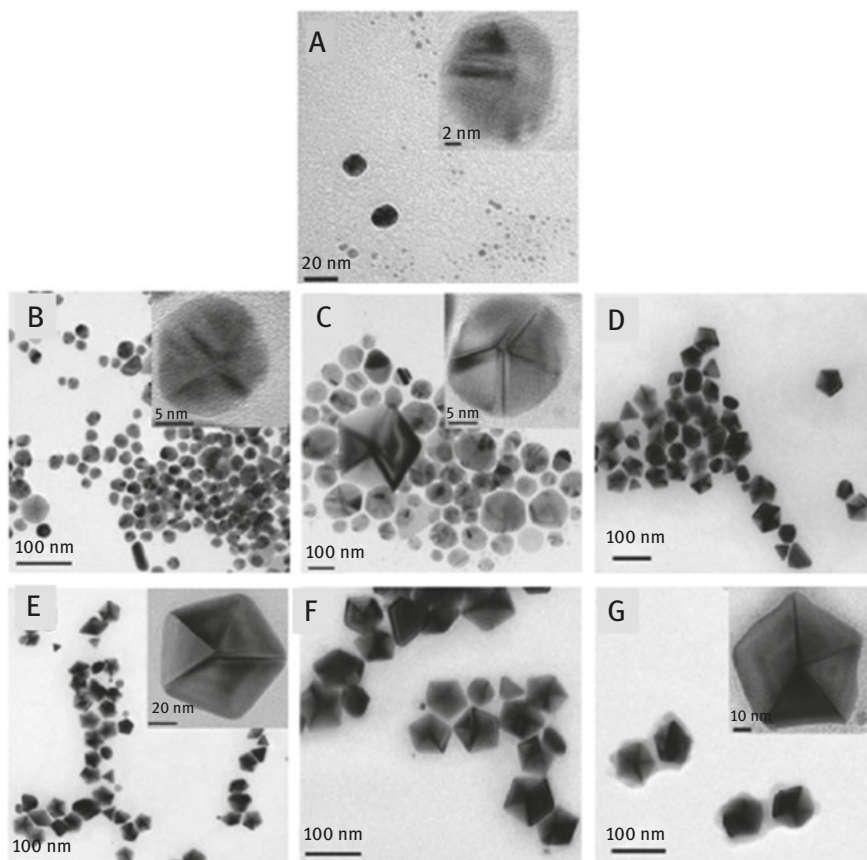


Figure 1.2: Time course of synthesis of decahedral AgNPs as revealed through TEM images at (a) 6 min, (b) 10 min, (c) 20 min, (d) 50 min, (e) 90 min, (f) 9 h and (g) 16 h (Reprinted with permission from ref. [32]. Copyright 2012, American Chemical Society).

the arrangement of atoms in a crystal. Thus, the SAED ring pattern over a selected area can be interpreted for determining the growth directions in a crystal and for phase identification. TEM image, SAED and dark-field images of icosahedral AgNPs synthesized via photo-assisted tartrate reduction method under UV (UV-B) irradiation over 48 h is shown in Figure 1.3 [33].

The brighter spots shown in Figure 1.3c can be grouped in concentric circles based on their distances from the centre. The radii of the circles were 2.67, 4.20, 5.79, 6.75, 7.39 and 8.38 nm⁻¹ and the d-spacings determined from these radii were 0.374, 0.238, 0.172, 0.148, 0.135 and 0.119 nm, respectively. The d-spacing of 0.238, 0.148 and 0.119 nm corresponds to the {111}, {220} and {222} facets of AgNPs, respectively. Spot A was attributed to the {311} facets. These observations were also supported by the XRD spectrum [33].

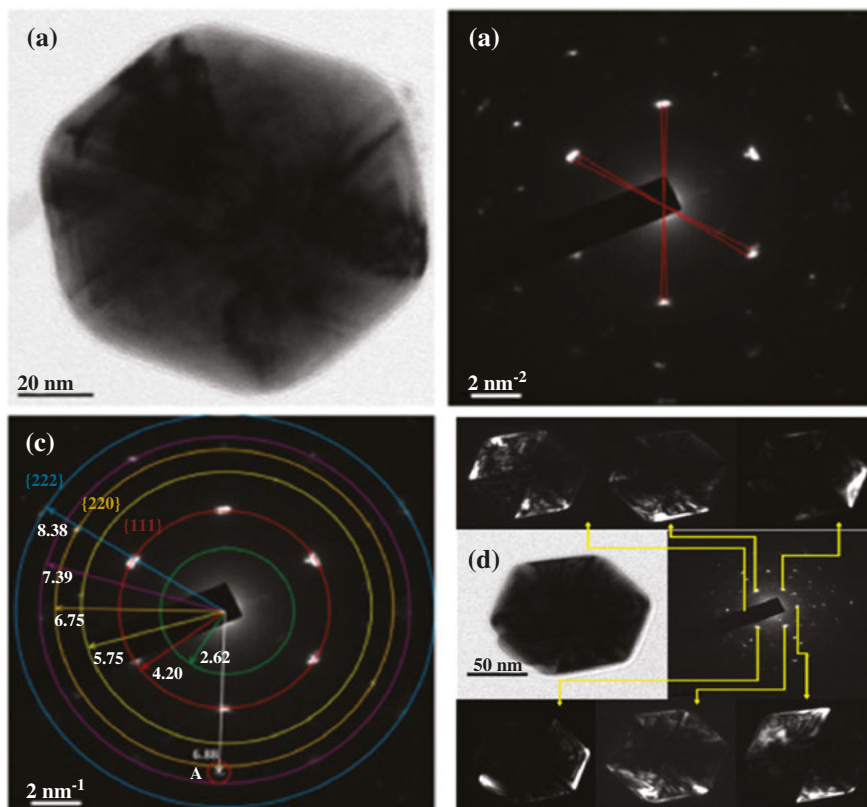


Figure 1.3: (a) TEM image (b) SAED pattern (c) assignments based on SAED (d) dark-field image and SAED pattern of an icosahedral AgNP (Reprinted with permission from ref. [33]. Copyright 2016, John Wiley and Sons).

1.2.3 Scanning electron microscopy and energy dispersive spectroscopy

SEM reveals the external morphology and texture and also provides insight on chemical composition of the surface and orientation of nanomaterial on the surface. Spatial variation in properties is illustrated through a two-dimensional image generated by scanning the specimen surface over a selected area using the signals from both secondary electrons (SE) and backscattered electrons (BSE). These electrons are generated from the surface of the specimen upon exposure to the electron beam irradiation. While inelastic collision and consequent scattering of the incident beam generates SEs, BSEs are produced by elastic collision followed by scattering. SEs, generally characterized by energy less than 50 eV, are effective in revealing the surface topography and morphology while BSEs are useful for demonstrating the contrasts that aids the visualization of samples containing multiple phases. BSEs can

also be used to resolve atomic number contrast as well as topographical contrast with a resolution of more than 1 μm .

High-energy electron beam irradiation of a sample also generates an X-ray signal that can be employed to gain information regarding chemical composition of the specimen. The X-ray signal originates from below the surface of the specimen and provides elemental and chemical composition based on the characteristic X-ray signals and the characteristic energy peak. The technique is known as energy dispersive X-ray analysis (EDX or EDAX). The basic principle of EDX is that the detector detects the characteristic X-rays emitted from a specimen surface when bombarded with a focused electron beam. The intensity of characteristic X-rays emitted due to each element present on a surface is a function of its mass concentration or atomic fraction. EDX analysis is comprised of a spectrum with multiple peaks, where the peak position (eV) reveals the elements present in a sample. SEM images and EDS spectra of AgNPs immobilized on a surface is illustrated in Figure 1.4a–d. [34] While the SEM micrographs (Figure 1.4a–c) illustrate the size, shape, morphology, texture and surface coverage of AgNPs on the surface, the EDX spectra (Figure 1.4d) confirms the presence of silver in the specimen by exhibiting the characteristic peak of silver at 3 keV. The adjacent image reveals elemental mapping of silver and other elements on the surface. Apart from silver, presence of carbon, oxygen and silicon was also observed.

1.2.4 X-ray crystallography

X-ray crystallography/diffractometry (XRD) is a method used for determining crystal structure of NPs. Crystalline NPs cause a beam of X-rays to diffract into specific directions. Based on the angle and intensity of the diffracted beam, a three-dimensional electron density map is produced for a crystal. The XRD spectra generated is a manifestation of the electron density map, such that, insights can be obtained regarding the position of atoms in a crystal. Moreover, XRD can yield information on chemical bonds, their disorders and various other useful information. The diffraction peak position and pattern helps in identification of the crystalline phases present and the mean crystallite size of NPs may be determined using Scherrer's formula: $D = k\lambda/(\beta \cos\theta)$ where, D = size of the NP, $k = 0.89$ (shape factor used for spherical NPs), $\lambda = 1.54056 \text{ nm}$ (X-ray wavelength for CuK_α), β is the line broadening, i. e., full width at half the maximum intensity (FWHM) expressed in radians, and θ is the angle obtained from 2θ value corresponding to an XRD peak. Peak broadening is inversely proportional to the size of the NPs; hence, significant peak broadening and correspondingly lower intensity of signals are found with smaller-sized NPs [35]. For AgNPs, a high-intensity diffraction peak at a 2θ value of 38.18° is commonly observed and it represents the (111) lattice plane of face-centred cubic (fcc) silver [36].

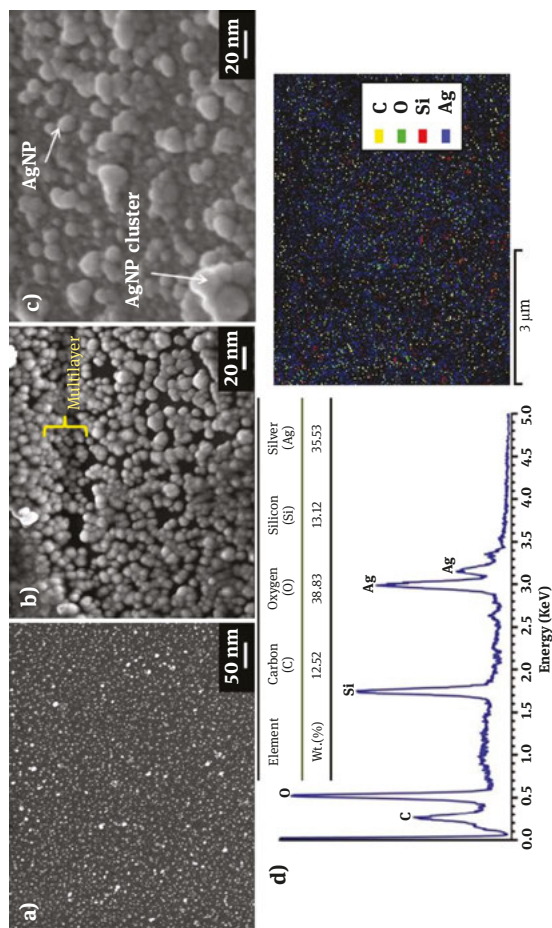


Figure 1.4: AgNPs immobilized on a glass substrate (a–c) FEG-SEM images, (d) EDX spectra (left image) and elemental mapping (right image) over an area (Reprinted from ref. [34]. Published by The Royal Society of Chemistry).

1.2.5 Fourier transform infra-red spectroscopy

In FTIR spectroscopy, as a sample is irradiated with infrared radiation, a part gets absorbed while the remaining is transmitted. The spectra generated based on molecular absorption and transmission represents a molecular fingerprint of the sample. It reveals unique molecular structures based on the functional groups present. This technique can be used to ascertain various unknown materials based on characteristic peak corresponding to a chemical species. It can also be used for determining the amount of components in a mixture depending on the vibrational spectra of the surface functional groups present in the sample. Its utility is illustrated through Figure 1.5 which depicts the presence of diverse functional groups in a leaf extract of *Skimmia lauriola* (A) and significant reduction in the abundance of various functional groups in the residual extract (B) after it was utilized for synthesis of silver NPs [37].

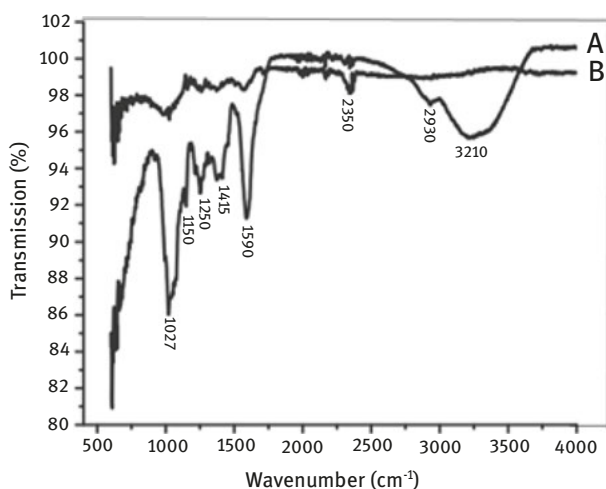


Figure 1.5: FTIR spectra of leaf aqueous extract of *S. laureola* before (A) and after (B) its use in AgNP synthesis. (Reprinted with permission from ref. [37]. Copyright 2015, Elsevier).

The various absorption peaks at wavenumbers, 1027, 1150, 1250, 1415, 1590, 2930 and 3210 cm^{-1} in the leaf extract corresponds to aliphatic amine (C–N stretch), alkyl halide (–CH X), aromatic amine (C–N stretch, C–C stretch), amine (N–H bend), alkane (C–H stretch) and carboxylic acid (O–H stretch), respectively. Reduction in these functional groups in the residual extract indicates the role of these biomolecules in AgNP synthesis.

1.2.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS), also referred as electron spectroscopy for chemical analysis (ESCA) is useful for surface characterization in terms of its

chemical state. XPS analysis is performed over average depth of approximately 5 nm. It is useful for determining the presence and chemical state of various elements associated with AgNPs synthesized as illustrated in Figure 1.6.

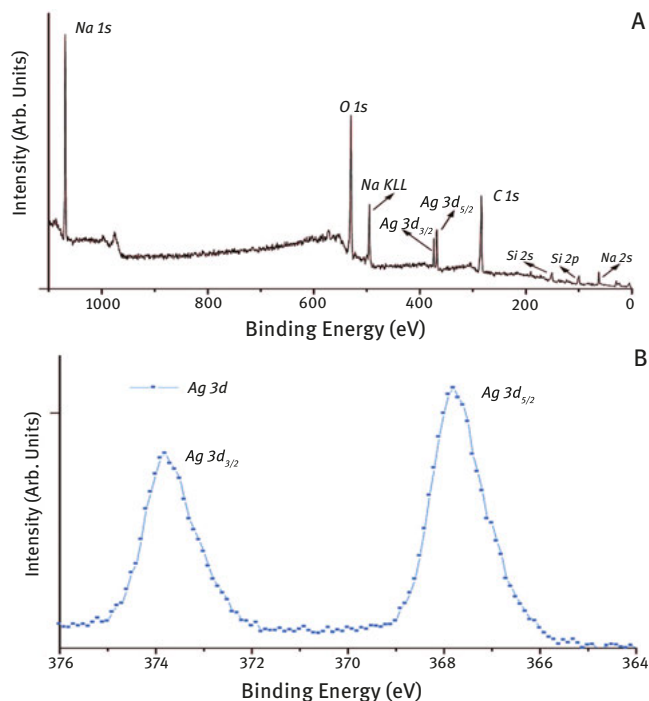


Figure 1.6: XPS spectra of AgNPs (A) Overall spectra and (B) Spectra due to Ag only (Reprinted with permission from ref. [38]. Copyright 2009, American Chemical Society).

The XPS spectra for AgNPs shown in Figure 1.6A exhibit characteristic peaks for Ag. The Ag (3d) region is characterized by a doublet with two peaks at binding energy of 373.8 and 367.9 eV (Figure 1.6B). These peaks may be attributed to spin-orbit coupling of Ag 3d_{3/2} and Ag 3d_{5/2}. The XPS spectra also reveals characteristic peaks due to presence of various other elements in the AgNPs, such as, Na (1s) at 1070 eV, O (1s) at 530 eV, Na (Auger KL₂₃L₂₃) at 495 eV and C (1s) at 284.5 eV that may be attributed to the presence of residual reducing and stabilizing agent associated with the AgNPs. No Ag₂O peaks are observed for the XPS spectra shown in Figure 1.6 [38]. In another study, the XPS spectra of AgNPs demonstrated peaks at 374.5 eV and 368.4 eV corresponding to Ag 3d_{3/2} and Ag 3d_{5/2}, respectively [34]. Deconvolution of the XPS spectra for Ag was found to reveal three additional peaks corresponding to binding energy of 367.7, 368.8 and 374.2 eV, confirming the presence of a small fraction of

AgO and Ag₂O along with metallic silver [34]. Thus, XPS analysis may reveal valuable information regarding the chemical nature of the surface.

1.2.7 Dynamic light scattering and zeta potential

Hydrodynamic size distribution and stability of NPs are important characteristics that should be determined after NPs are synthesized. DLS, also known as photon correlation spectroscopy (PCS), is widely used for determining the size distribution of NPs in a colloidal suspension. DLS works on the fact that NPs in colloidal dispersion move randomly due to Brownian motion and hence cause scattering of the incident light. The diffusive transport of NPs through a liquid of low Reynold's number can be explained by Stokes Einstein equation ($D = k_B T / 6\pi\eta R$, where, D denotes the translational diffusion coefficient, k_B is the Boltzmann's constant, R is the hydrodynamic radius of the particle and η is the dynamic viscosity of the solvent). The scattering of incident light is proportional to the 6th power of the radius of the NPs. When the size of NPs is less than 1/10th of the wavelength of incident light, elastic scattering referred as Rayleigh scattering occurs. In contrast, when the size of the NPs exceeds this threshold, inelastic and anisotropic scattering, referred as Mie scattering occurs. The scattering of light is dependent on various factors such as concentration, shape and size of the particles as well as the refractive index of the solvent. The scattering of light from individual NPs may get affected by other particles due to random Brownian motion of all the NPs in solution. At higher concentration, the inter-particle interactions also become significant as the number of collisions increase; however, the average path length travelled by the particles between successive collisions decrease [39].

Scattering of incident laser light is detected in DLS. The intensity of the scattered light show fluctuations due to the random motion of the NPs. Statistical analysis of such intensity variations can yield the diffusion coefficient, which is then used for estimating the hydrodynamic radius R as per Stokes Einstein equation. Hydrodynamic radius is typically much larger than the radius of the NPs determined through TEM. DLS measures size distribution of NPs in a colloidal dispersion based on intensity of scattered light whereas in TEM a direct measure of particle size is obtained from the image of the NP and size distribution may also be obtained through image analysis of a sufficiently large number of NPs. In addition, while DLS measures the hydrodynamic radius, TEM captures images of NPs based on the projected surface area by the incident electrons transmitted through the sample in dry condition, under high vacuum. The advantage of determining size distribution using DLS is that it provides the size distribution based on measurement of millions of NPs. In contrast, TEM gives size distribution based on only a few hundred NPs. Hence, DLS can be a preferred choice when determination of size distribution and polydispersity is a primary objective [39]. For non-spherical NPs, the hydrodynamic radius obtained is a hypothetical value, and

in some cases, e. g., cylindrical NPs, the length, diameter and aspect ratio can also be derived from the hypothetical radius.

Presence of charge (+/–) on the surface of NPs impart stability to the NPs and prevents aggregation over time due to electrostatic repulsion between particles carrying like charges. This is achieved using appropriate stabilizing agents during the synthesis of NPs as discussed in later sections. The charge on the surface of NPs is indicated by the zeta potential, since the exact potential on the particle surface, i. e., Nernst potential cannot be directly measured. Zeta potential of NPs is the potential at the plane of shear/slipping plane. An electric double layer (EDL, comprising of the Stern layer and Gouy Chapman layer) enriched in oppositely charged ions forms around charged particles in solution. When a charged particle moves in an electric field, a part of the EDL up to the slipping plane moves with it. The potential developed on the slipping plane, i. e., zeta potential, can be determined based on electrophoretic mobility. Often DLS instruments have provision for determination of zeta potential also. During electrophoresis, NPs scatter the incident laser beam. The scattered beam from mobile NPs have different frequency than the incident laser light and the frequency shift is proportional to the velocity of the NPs. Zeta potential can be determined based on this velocity. It may be emphasized that although zeta potential reflects the particle surface charge, it is also affected by water chemistry, i. e., pH and ionic strength of the solution (I). Depending on the ionic strength, the value of zeta potential may change, i. e., the zeta potential becomes less negative for negatively charged particles as “I” increases, even when the particle surface charge remains unaltered [40]. NPs with magnitude of zeta potential exceeding 25 mV is reported to demonstrate a high degree of stability [41]. When AgNPs synthesized are characterized by low zeta potential values, they are found to aggregate spontaneously due to Van der Waal interactions. Thus, determination of zeta potential gives insight on stability of the NPs formed.

1.3 Synthesis of silver NPs

Primarily two approaches are used for fabrication of metal NPs, i. e., top-down approach and bottom-up approach (Figure 1.7). The former deals with the synthesis of NPs using a bulk material, in which NPs are directly generated from the bulk material using techniques such as milling, pyrolysis and photolithography [42]. The size of NPs produced using these approaches are between 10 and 100 nm. The surface structures commonly show imperfections that adversely affect the physical and chemical properties of the NPs. Thus, top-down approach cannot be gainfully applied in most applications. Bottom-up approach involves the construction of complex clusters and NPs starting from individual atoms, molecules or clusters by employing processes, such as, chemical reactions coupled with nucleation and growth processes [42].

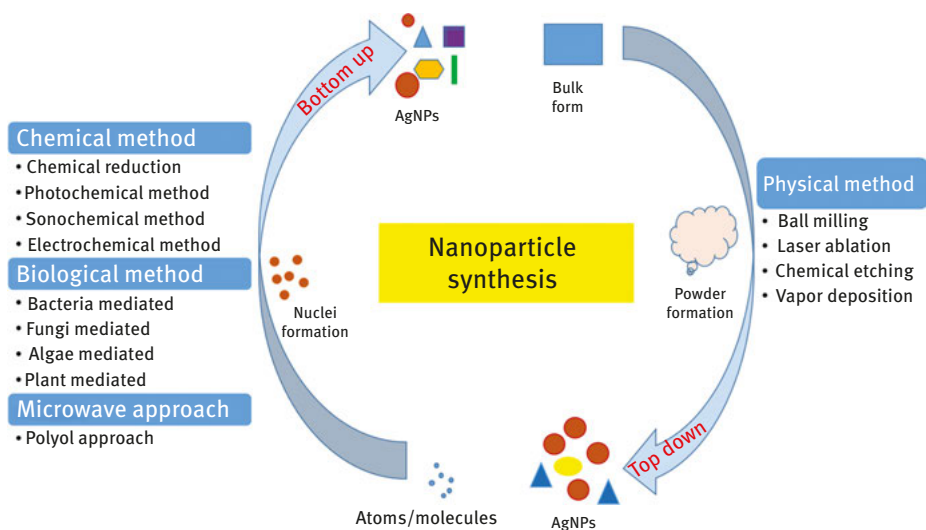


Figure 1.7: Nanoparticle synthesis: top-down approach versus bottom-up approach.

1.3.1 Top-down approaches

The top-down synthesis route involves synthesis of nanomaterials by breaking down the bulk material using various physical forces. The physical energy for size reduction may be applied as: mechanical energy that is utilized in processes, such as, ball milling, crushing or grinding; electrical energy that is utilized in processes, such as, electrical arc discharge method, high-energy laser ablation method, or as photon beams; and thermal energy, such as in pyrolysis. A detailed discussion is provided in the subsequent sections.

1.3.1.1 Physical method

The predominant physical processes are classified as mechanical processes and vapour-based processes. Mechanical methods involve high-energy ball milling techniques, which can be achieved in mills such as planetary, vibratory, rod or tumbler-based mills. Vapour-based techniques include pyrolysis, physical vapour deposition, electric arc discharge and laser ablation. In pyrolysis, an organic precursor (liquid/gas) is forced through a vent at elevated pressure and burnt. Oxidized NPs may be recovered from the ash generated. In the evaporation/condensation method, metal NPs are usually synthesized in a tube furnace maintained at atmospheric pressure. The material of interest is vaporized into the carrier gas from the precursor placed in a boat held within a furnace. Diverse types of NPs including AgNPs have been successfully synthesized using the evaporation/condensation

technique. The advantage of physical methods includes uniform size distribution of NPs and high purity of the NPs formed [43].

1.3.1.1.1 Ball milling/attrition

The attrition/ball milling technique consists of a container filled with hardened steel or tungsten carbide balls and air or inert gas, where the material of interest is fed as flakes maintaining a specific mass ratio of balls to the desired material. The container is rotated at a high speed around a central axis, where the desired material is forced to move towards the wall and pressed against it. The factors that can be controlled to produce NPs with desired characteristics include varying the speed of rotation, duration of milling to grind the material and the atmospheric medium, which give rise to NPs of size range of a few nm to few tens of nm. In case of melt mixing method, the NPs formed are arrested in glass, an amorphous solid lacking symmetric arrangement of atoms/molecules. The basic principle is that when metals are cooled at a very high cooling rate (10^5 – 10^6 K/s), the metals can form amorphous solid metallic glasses. The mixing of molten streams of metals at very high velocity with turbulence leads to the formation of NPs.

Khayati and co-workers [44] synthesized silver nanopowder of average size 28 nm in a high-energy planetary ball mill by mechanochemical reduction of Ag_2O (5–40 μm) using 40 mol% excess graphite (10–50 μm) as reducing agent. Excess graphite acted as a diluent and facilitated maximum interaction between the precursors during synthesis. The parameters affecting synthesis using ball mill machine were: rotation speed of the disc of diameter 350 mm (250 rpm), rotation speed of hardened chromium steel vials of 90 mm diameter having 150 ml capacity (450 rpm), ball (20 mm diameter, made up of hardened carbon steel) to powder weight ratio (20:1) and time of milling (0–22 h) in dry milling condition with total powder mass of 9.75 g. With increase in milling time, the Ag_2O peak in XRD spectra gradually broadened and its height decreased and Ag peaks in the XRD spectra appeared between 3 and 6 h of milling [44]. Thus, the reduction reaction was initiated after a period of 3 h. Moreover, increase in intensity of the Ag peaks was obtained on further milling and a single phase of Ag was obtained only after milling for 22 h. The rate of transformation decreased at the end of milling process, i. e., beyond 22 h. Thus, the reduction process started with a nucleation phase and was followed by a growth phase. The activation energy for nucleation depends on the degree of deformation. In this case, the energy barrier got reduced due to the large number of imperfections generated by mechanical milling. Larger amount of nuclei was generated after 6 h of milling and hence synthesis of AgNPs was enhanced as large amount of reactants were available for reduction. Thus, the AgNP synthesis rate improved, such that 72% reduction of Ag_2O occurred during 6–16 h of milling.

Cryomilling is a variation of the ball milling technique, where ball milling is performed at a very low temperature (i. e., $-160 \pm 10^\circ\text{C}$) under an inert argon

atmosphere. Conventionally, it can be achieved by mixing the silver powder with liquid nitrogen (LN) during ball milling to achieve a lower temperature. However, the mixing of LN with silver powder during ball milling process poses a challenge. Kumar et al. [45] synthesized highly pure spherical AgNPs (size: 4–8 nm, with impurities <35 ppb) using an advanced version of cryomill containing a single tungsten carbide (WC) ball over 7 h. The ball to silver powder (40 μm) ratio was maintained at 80:1. The surfactant-free AgNPs synthesized were found to be thermally stable and could withstand a temperature up to 350°C, whereas AgNPs synthesized through traditional ball milling technique are reported to coalesce at 200°C and form micron-sized silver particles within just 30 min of annealing. In contrast to conventional cryomilling, this custom-built cryomill did not require direct mixing of LN with the silver powder during ball milling. The custom-built cryomill had a special reservoir surrounding the milling chamber which was maintained at –160°C during the milling process. This approach could generate large quantity of AgNPs in a single ball mill i. e., ~60–70 g/day. The extremely low temperature used in cryomilling provided additional advantages. Cooling the silver powder and milling ball facilitated the formation of finer grain structure, accelerated the fracturing process and suppressed the recovery and recrystallization of particles such that size-controlled AgNPs (6 ± 2 nm) could be formed.

1.3.1.1.2 Physical vapour condensation

For NP synthesis, the vaporization method has been widely used. In this method, the target materials are evaporated by a heat source followed by rapid condensation. Based on the reactions, the vaporization process can be divided into physical and chemical methods. Physical vapour condensation (PVC) methods are used when the resultant NPs have the same composition as the target material. However, when NPs have to be of different composition than the target, chemical vapour condensation (CVC) method is used. In CVC, the vapour and other system components react with each other during the vaporization and condensation processes [46].

1.3.1.1.3 Electrical arc-discharge method

The electrical arc discharge method can produce high-purity NPs and is also characterized by high yield. It is a cost effective and environment-friendly method that utilizes a DC power supply and an open vessel containing either ultra-pure/deionized water, or alcohol [47, 48]. Tien et al. [47] synthesized AgNP suspension in water using DC arc-discharge between two silver electrodes immersed in pure water [49]. During arc-discharge, the Ag electrodes used were etched in the aqueous medium and the surface layer was vaporized due to the very high temperature (~1000°C) in the vicinity of the electrodes. Subsequently, the metal vaporized was condensed as AgNPs in the dielectric liquid. To effectively ionize the aqueous medium between the electrodes, a pulse voltage of 70–100 V was applied for 2–3 ms using the DC arc-discharge system and the voltage was later lowered to 20–40 V for around 10 ms.

AgNP formation in this system was facilitated by four effects, i. e., the strong electric field, a high temperature plasma, release of active silver atoms from the silver electrodes and release of hydrogen and oxygen atoms from water molecules. The AgNPs initially formed upon condensation were positively charged such that atomic oxygen was attracted to it and water molecules also formed hydrogen bonds with the oxygen on the surface (shown as dashed line in Figure 1.8). This resulted in a thermodynamically stable colloidal suspension of AgNPs, of average size 20–30 nm [49].

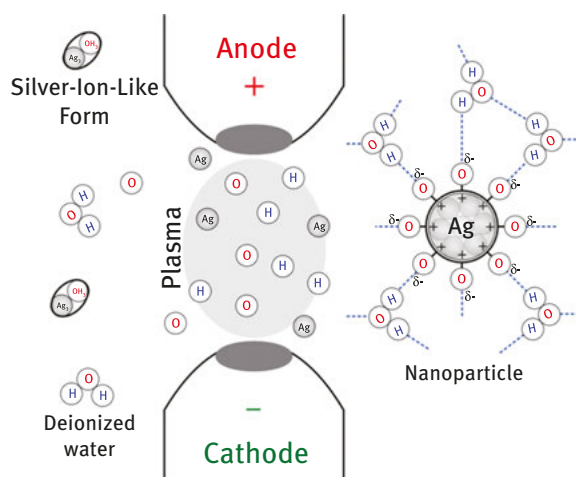


Figure 1.8: Plasma and electrical discharge contributing to the formation of a stable suspension of AgNPs (Reprinted with permission from ref. [49]. Copyright 2008, Elsevier).

Rashed [48] also synthesized AgNPs using this method by applying a stable voltage of 130 V between two silver electrodes immersed in deionized water maintaining a distance of ~1 mm between the electrodes. The short distance between the electrodes caused generation of electric spark which caused passage of ~35 mA electric current through the water. The silver atoms vaporised from the anode surface later condensed in water to form AgNPs of size ~8.4 nm through nucleation mechanism.

1.3.1.1.4 Laser ablation method

The laser ablation technique illustrated in Figure 1.9 involves generation of non-equilibrium vapour/plasma at the surface of a material using a strong laser pulse. It differs from the laser evaporation process where heating and evaporation of material occurs under equilibrium conditions. A high-power pulsed laser together with an ablation chamber [50] is used in the laser ablation device. The temperature of the target is elevated due to absorption of the high-power laser beam which causes vaporization of atoms from the surface of the target into the laser plume.

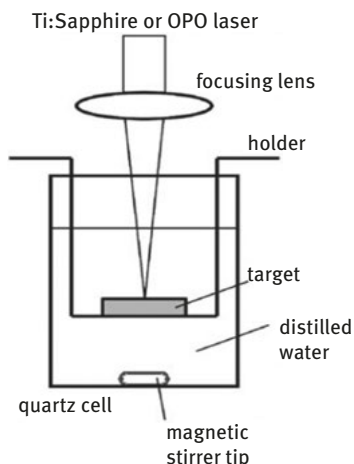


Figure 1.9: Schematic illustrating laser ablation in solution (Reprinted with permission from ref. [50]. Copyright 2002, Elsevier).

The vaporized atoms may either condense as clusters and particles without any chemical reaction or may react in the vaporized state to yield new materials. The condensed particles may be collected through deposition on a substrate or by passage through a glass fibre mesh-type filter.

Synthesis of spherical AgNPs have been illustrated using both nanosecond and femtosecond laser pulses using apparatus as illustrated in Figure 1.9. However, although femtosecond laser pulses yielded AgNPs with narrower size distribution (20–50 nm), its efficiency was found to be lower [50]. The ablation efficiency in air and water medium has also been compared for these two types of laser. While nanosecond laser ablation resulted in comparable efficiency irrespective of the medium, femtosecond laser yielded higher efficiency in air compared to water [51]. Apart from duration of laser pulse and use of air/water media, other factors that influence the ablation efficiency and characteristics of the AgNPs formed are wavelength and fluence of the laser, duration of the ablation process and the presence of surfactants in liquid media [43]. Only a sufficiently high laser fluence (power) can eject metal particles from the target. However, as fluence increases, the size of NPs formed also increases. Thus, the minimum threshold fluence is commonly used for generating small NPs. The wavelength of the laser and time duration of irradiation also controls the concentration and morphology of the NPs formed. NP concentration increases with increase in irradiation time until a saturation value is reached. In a highly concentrated colloidal suspension of NPs, light absorption is adversely affected, leading to saturation in concentration of the NPs.

The effect of laser wavelength on the size of AgNPs formed is illustrated in Figure 1.10 based on a study conducted by Tsuji et al. [50]. They found that AgNPs prepared using lower wavelength laser yielded AgNPs with narrower size distribution. The mean size of AgNPs formed was significantly different at

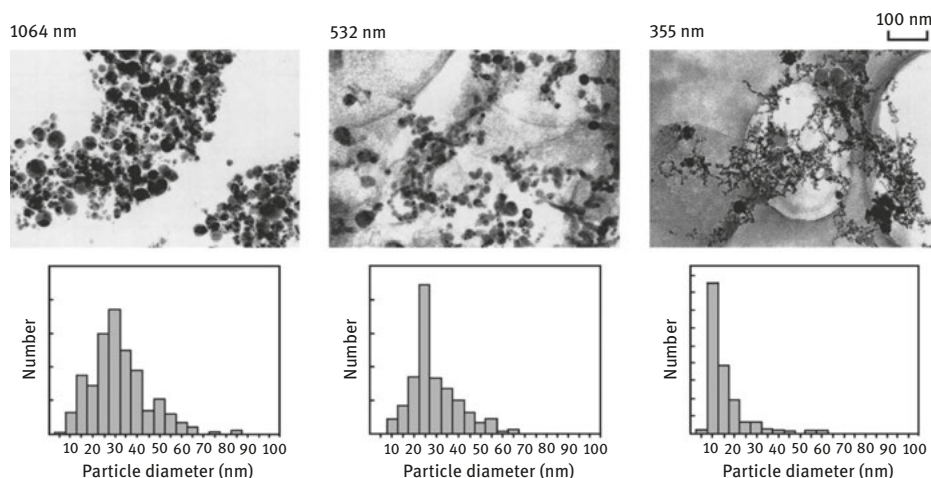


Figure 1.10: TEM images of silver particles in colloidal solution prepared by laser of varying wavelength (100, 1000X). (Reprinted with permission from ref. [50]. Copyright 2002, Elsevier).

532 nm (26 ± 11 nm) and 355 nm (12 ± 8 nm) (Figure 1.10). Alteration in laser wavelength affects the ablation efficiency, self-absorption and penetration depth of the laser beam such that the mean size and size distribution of NPs formed is altered. The characteristics of NPs formed by laser ablation in an aqueous medium is also affected by the type and concentration of surfactants added to the medium. Smaller NPs can be formed by increasing the surfactant concentration [43].

In a study by Mafune et al. [52], AgNPs were synthesized using laser ablation on a silver plate immersed in an aqueous solution containing a surfactant, e. g., sodium dodecyl sulphate (SDS). The surfactant was used to prevent aggregation of the NPs. It surrounded each NP thereby preventing them from coming in direct contact with each other. Synthesis of AgNPs was accompanied by irradiating the silver plate placed in 10 mL aqueous solution of SDS in a glass beaker. Irradiation was done using 532 nm Nd:YAG laser (operated at 10 Hz, using a lens with focal length 250 mm) and varying output power of 40, 55, 70 and 90 mJ/pulse. For output power of 90 mJ/pulse, the diameters of AgNPs synthesized were 16.2 ± 4.0 , 14.9 ± 8.4 and 11.7 ± 5.3 nm for SDS concentration of 3, 10 and 50 mM, respectively. Thus, a gradual decrease in size of AgNPs was observed with increase in surfactant concentration. For AgNPs synthesized at constant SDS concentration of 10 mM with variable output power, the diameters of AgNPs formed were 7.9 ± 3.3 , 10.7 ± 5.8 and 12.8 ± 4.1 nm for power output of 40, 55 and 70 mJ/pulse, respectively. AgNP synthesis using laser ablation was also attempted using dodecanethiol solution in heptane. Synthesis of AgNPs was revealed through colour change of the solution to light brown observed after 10 h and TEM micrographs revealed synthesis of AgNPs with size range 5–30 nm.

Dodecanethiol solution in heptane generated significantly lower yield of AgNPs compared to aqueous solution of SDS. Thus, the concentration and type of surfactant, solvent used and power output of the laser plays an important role in determining the yield and the characteristics of the AgNPs synthesized.

Bae et al. [53] fabricated AgNPs using pulsed laser ablation of a target silver plate placed in the bottom of a glass vessel containing NaCl solution. AgNPs were synthesized by laser irradiation of a silver plate with 1 mm spot size using Nd: YAG laser beam (wavelength: 1064 nm, 5 ns pulse). Effect of NaCl concentration (5–20 mM) on AgNP synthesis was also tested. Maximum yield of AgNPs was observed for 5 mM NaCl concentration and the AgNPs synthesized had average size of 26 nm (range: 5–50 nm). The absorbance due to LSPR (at $\lambda_{\text{max}} = 400$ nm) increased from 0.86 to 1.45 with increase in NaCl concentration from 0 to 5 mM; however, the FWHM decreased over this range. The increase in yield, smaller size of the AgNPs formed and greater aggregation tendency observed were attributed to the presence of chloride ions. Increase in absorbance at λ_{max} was not observed when NaCl was added after AgNPs were synthesized in pure water. However, AgNPs prepared in pure water exhibited better stability as compared to those synthesized in NaCl solution. Increase in NaCl concentration beyond 5 mM caused further decrease in stability of the AgNPs synthesized and promoted aggregation.

Silver NP synthesis through laser ablation in organic solvent was reported by Amendola et al. [54]. Synthesis of AgNPs was performed using a silver plate within a cell containing the solvent. Laser ablation was performed with 1064 nm Nd:YAG laser pulses (9 ns pulses for 10 min) with output power of about 10 J/cm². Various organic solvents such as, acetonitrile, N,N-dimethylformamide, tetrahydrofuran and dimethyl sulfoxide were used for AgNP synthesis. Spherical and crystalline AgNPs with average size of 1.9 ± 1.5 nm and 2.2 ± 2.5 nm were synthesized in acetonitrile and dimethylformamide, respectively. However, a few nm thick amorphous shell was observed surrounding the AgNPs synthesized in tetrahydrofuran. Average size of the core AgNPs was found to be 2.4 ± 1.1 nm, whereas the thickness of the amorphous shell varied from sub-nanometre to several nanometres. AgNP synthesis could also be achieved in dimethyl sulfoxide and the average size of AgNPs formed was determined as 3.9 ± 1.9 nm.

In a recent study by Sebastian et al. [55], AgNPs were synthesized by laser ablation using a silver plate placed within ethanol containing PVP as stabilizing agent. They also explored laser-induced transformation of spherical AgNPs. Initially spherical AgNPs were synthesized using 1064 nm Nd-YAG laser (9 ns pulses) as the source and laser ablation was conducted for 20 min in an ethanolic solution of PVP (6 M, MW 10,000). Stable spherical AgNPs (average size: 45 nm) having fcc crystal structure were obtained. The spherical AgNPs synthesized were subjected to structural transformation by irradiating the solution with 532 nm laser. After 45 min of irradiation with 532 nm laser, a colour change from light to dark

yellow was observed in the colloidal AgNP solution. TEM micrographs revealed fragmentation of almost all larger AgNPs (size: 45 nm) into smaller fragments of size up to 4 nm. Upon irradiation using 532 nm laser for up to 9 h, the fragmented NPs (of size range 1–4 nm) assembled to produce stable Ag nanorods (average width 160 nm, length 8.7 μm and average aspect ratio: 54). However, since PVP restricted growth along specific crystallographic facets, it also facilitated transformation of the nanorods to nanowires. Hence, a mix of nanorods and nanowires was obtained upon ripening the PVP solution.

In general, top-down approaches for AgNP synthesis has various limitations, such as, consumption of large amount of energy that is required for raising the temperature around the source material. Correspondingly large time duration is required for achieving thermal stability. Moreover, most of the synthesis methods discussed in the preceding section are less amenable for synthesis of size- and shape-controlled AgNPs. Hence, bottom-up AgNP synthesis approaches are often preferred. These approaches are discussed in the following section.

1.3.2 Bottom-up approaches

Crystal growth is a bottom-up approach, where atoms, ions or molecules are assembled into the desired crystal structure on a growth surface. The size of the NPs synthesized using the bottom-up approach covers the full nano scale. Bottom-up approaches for NP synthesis improves the probability of achieving specific shape and size, reduces defects in the crystal structure and can provide greater homogeneity in chemical composition. Since NPs are synthesized by reducing the Gibbs free energy, they remain in a state that is closer to thermodynamic equilibrium [56]. Therefore, bottom-up approaches are found more useful and are widely used for synthesis of AgNPs.

As illustrated in Figure 1.11, two main reaction phases completes the formation of AgNPs in the bottom-up approach: nucleation, i. e., the formation of nuclei; and growth of NPs through coagulation and coalescence processes. During synthesis of NPs, aggregation (coarsening) through either Ostwald ripening or agglomeration over time is a spontaneous phenomenon since it reduces the surface to volume ratio. To synthesize NPs of controlled size, a key challenge is to overcome the large surface energy of the NPs and resist aggregation [57, 58]. The nature of the formulation and various process parameters, such as, temperature, reaction time, pressure and degree of mixing can be optimized to control the growth of NPs. The formulation typically contains diverse chemicals serving as precursor salt, reducing agent and stabilizing agent/capping agent. The composition of the formulation and concentration of various chemicals along with the order of addition may affect the process as discussed in later sections. The commonly used bottom-up methods include chemical reduction and biological reduction of a precursor salt. Biological

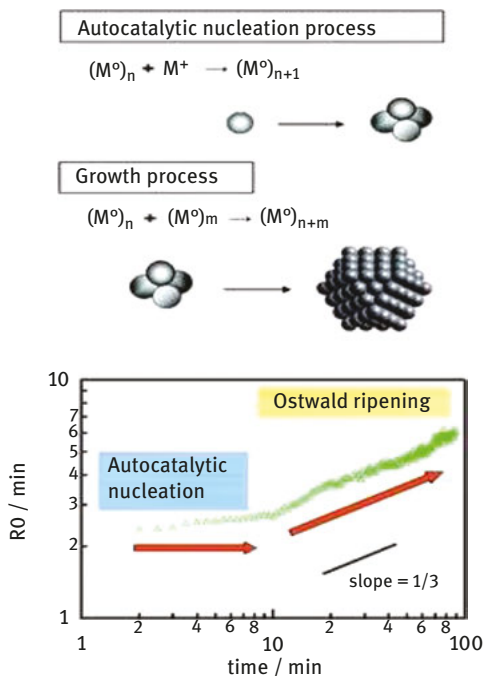


Figure 1.11: Change in particle radius and proposed mechanism for formation of silver nanoparticles (Reprinted with permission from ref. [57]. Copyright 2010, American Chemical Society).

reduction commonly relies on microbial enzymes, extracellular polymeric substances and other components that are released into the culture broth or involve the use of plant extracts [59, 60]. Chemical reduction [29, 61, 62] is commonly facilitated by heating while biological reduction may proceed under ambient conditions due to presence of enzymes that serve as biocatalysts. Although commonly coupled with conventional heating, chemical reduction is also sometimes coupled with alternative energy sources, and the processes are subsequently designated based on the energy source used. These include electrochemical methods [63], photochemical methods [64], sonochemical methods, γ -radiation-based methods [65] and microwave-based methods. A detailed description of various bottom-up synthesis approaches is provided in subsequent sections with specific reference to size- and shape-controlled synthesis of AgNPs.

1.3.2.1 Mechanism of bottom-up synthesis of shape- and size-controlled silver NPs

Most of the bottom-up techniques result in synthesis of spherical NPs. However, recently there is much interest in shape-controlled synthesis and researchers have successfully demonstrated synthesis of NPs with specific shape using chemical and photochemical method. Synthesis of AgNPs via bottom-up approach requires a metal

precursor salt, a reducing agent and a stabilizing/capping agent. The most commonly used Ag precursor salt is silver nitrate (AgNO_3) [66] whereas, sodium borohydride (NaBH_4) [67], polyol (ethylene glycol, EG) [68] or sodium citrate (TSC) [69] is frequently used as reducing agent. Use of various stabilizers/capping agents, such as, TSC [70], cetyltrimethylammonium bromide (CTAB) [67], bis(p-sulfonatophenyl)phenyl phosphine dipotassium dehydrate (BSPP) [70], polyvinylpyrrolidone (PVP) [68], polyacrylamide (PAM) [71], poly((sodium styrenesulfonate) (PSSS) [72], chitosan [73] and SDS [74] have been reported. The nucleation and growth of NPs is governed by various reaction parameters, such as, reaction temperature, pH and type of precursor, reducing agent and stabilizing agent, precursor concentration, molar ratio of surfactant/stabilizer and precursor [75]. In general, nuclei formation is achieved by reduction of the metal precursor salt by the reducing agent. This may either be achieved directly by the reducing agent or the process may be assisted by providing energy in various forms including conventional heating, microwave heating and light energy. The nuclei generated undergoes growth process through Ostwald ripening followed by coalescence leading to the formation of NPs. However, as already highlighted, the NPs may aggregate over time. Stabilizing/capping agents are required to prevent aggregation of the NPs. Stabilization can be achieved either through electrostatic or steric repulsion. Electrostatic stabilization is usually achieved through anionic species, such as, citrate, halides, carboxylates or polyoxoanions that adsorb or interact with the AgNPs to impart a negative charge on the surface. The surface charge on the AgNPs produces an EDL resulting in coulombic repulsion between the NPs. Steric stabilization can be achieved by interaction of NPs with bulky groups, such as, organic polymers and alkylammonium cation that prevent aggregation through steric repulsion [43]. Addition of stabilizers or surfactants may also facilitate directed growth of NPs thereby generating NPs of specific shape. Selective adsorption of the surfactant/stabilizer to specific crystal facets constraints the growth along specific crystal axes resulting in the synthesis of NPs characterized by distinct shape [76]. The various approaches towards control of size and shape are discussed in the following sections.

1.3.2.1.1 Chemical reduction

Three major group of methods are reported for shape- and size- controlled synthesis of AgNPs based on the reducing agent employed, i. e., polyol -based synthesis, citrate-based synthesis and borohydride-based synthesis. The specific shapes that have been synthesized through these three broad group of methods are illustrated in Figure 1.12, Figure 1.13 and Figure 1.14.

Polyol-based synthesis has been extensively studied for achieving various shapes and sizes of AgNPs. Spherical AgNPs of average size 10–30 nm can be obtained by proper choice of PVP to AgNO_3 mass ratio (such as, 2:1) [77, 78] and is sometimes facilitated by using ammonia in the formulation. Wiley et al. [79] explored variations of the polyol method for synthesizing AgNPs of diverse shapes, such as, pentagonal

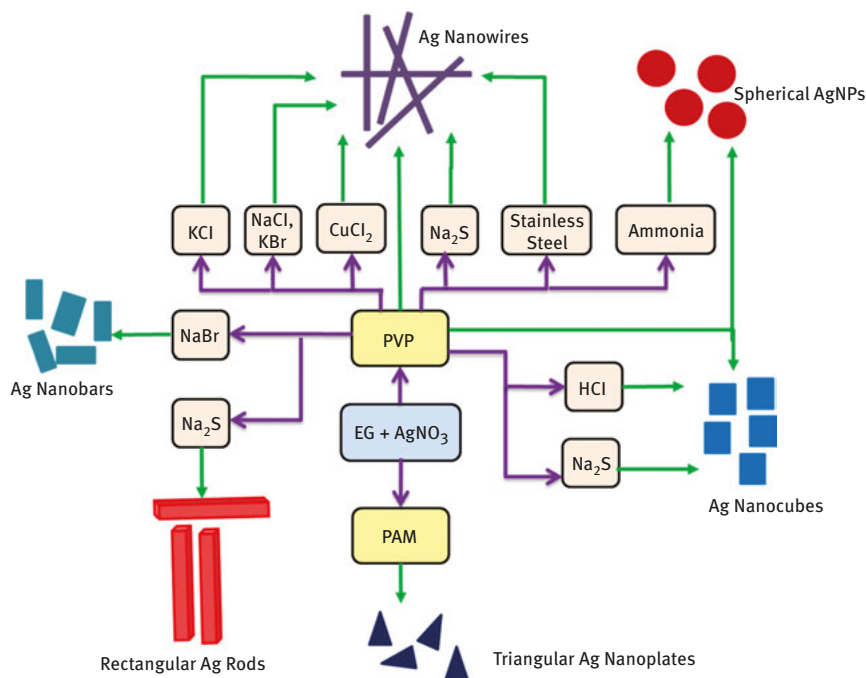


Figure 1.12: Schematic demonstrating AgNP synthesis via chemical route using polyol -based methods highlighting the various shapes that can be achieved through appropriate choice of reagents.

AgNPs, nanowires, cuboctahedra, nanocubes, nanobars, bi-pyramids and nanobeams. In a typical polyol method, EG, AgNO₃ and PVP are used as the polyol, salt precursor and polymeric capping agent, respectively. At elevated temperature, silver ions are reduced by EG to silver atoms and subsequently nuclei are generated. These nuclei grow to form multiply twinned, singly twinned or single-crystal seed as shown in Figure 1.15. These seeds grow to yield nanostructures of diverse shapes.

Crystallinity of the seeds plays a critical role in controlling the shape of AgNPs and Ag nanostructures [79]. In the presence of controlled amount of chloride and iron impurities, multiply twinned decahedral seeds grow to form nanowires whereas single crystal seeds grow to form silver nanocubes. When NaCl is replaced with NaBr and a specific NaBr concentration is employed, single crystal seeds grow into nanobars and seeds with a single twin plane grow to produce right bipyramids. In this approach, PVP facilitates synthesis of shape-controlled AgNPs by binding strongly with {100} crystal facets of the seed. This allows directed growth of AgNPs and yield AgNPs with specific shapes.

Presence of Na₂S in polyol-based synthesis can generate nanowires, nanocubes and rectangular nanorods. On addition of Na₂S, Ag₂S produced in the early stage helps to reduce the concentration of Ag⁺ ions in the initial stage and thus controls the

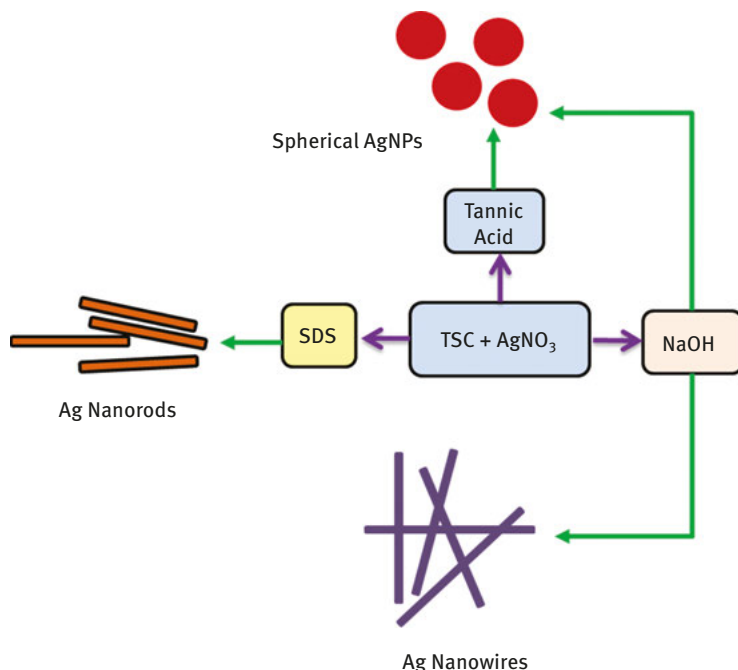


Figure 1.13: Schematic demonstrating AgNP synthesis via chemical route using citrate-based methods highlighting the various shapes that can be achieved through appropriate choice of reagents.

formation of silver seeds. In a successive reaction, Ag⁺ ions from Ag₂S colloids are released into the solution [80]. This facilitates nanowire formation. The length and diameter of the nanowires can be adjusted by controlling the Na₂S concentration [80]. By lowering the surface energy of {100} facet of the seeds by controlling the PVP concentration and by controlling the concentration of sulfide ions (28–30 μM) at a temperature of 150–155°C, nanocubes can be obtained in less than 10 min [81]. Rectangular nanorods can be synthesized by maintaining molar ratio of PVP to AgNO₃ at 0.93 and by increasing the reaction time sufficiently [82]. Nanowires can be synthesized upon addition of CuCl₂ and KCl in polyol-based synthesis. This is facilitated by formation of AgCl nanocrystallites that reduces free Ag⁺ ions during the initial stages of Ag seed formation. The subsequent slow release of Ag⁺ ions helps in ensuring high yield of multiply twinned Ag seeds necessary for nanowire synthesis [83, 84]. However, the nanowires formed have narrower diameter when grown in the presence of bromide ions [85].

Using TSC as reducing agent (Figure 1.13), spherical AgNPs and Ag nanowire can be produced by controlling the pH of the reaction mixture with NaOH [69, 86]. Nanowires are formed at pH 6.5. Formation of spherical AgNPs is facilitated by rapid nucleation at solution pH slightly above neutral (7.7) followed by lowering the pH to 6.1 during the growth stage. SDS plays an important role in nanorod synthesis. SDS

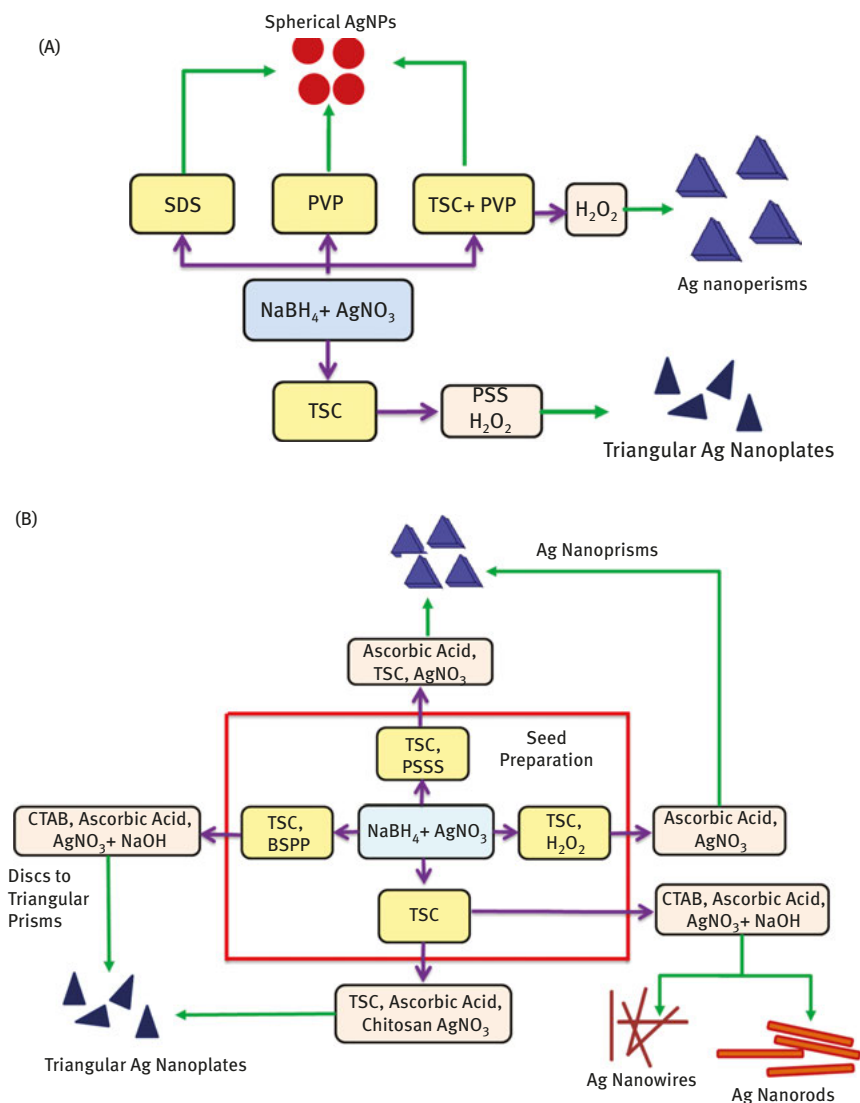


Figure 1.14: (A, B): Schematic demonstrating AgNP synthesis via chemical route using borohydride-based method highlighting the various shapes that can be achieved through appropriate choice of reagents.

micelles are produced in aqueous solution when its concentration exceeds the critical micelle concentration (CMC). The shape of the micelle depends on SDS concentration. As SDS concentration increases, the shape of the micelles changes from spherical to cylindrical. The AgNPs growing inside SDS micelles also takes the shape of the micelles, such that nanorods are formed at higher SDS concentration [74].