Silver nanowires (AgNWs) have a broad range of applications including nanoelectronics, energy conversion, health care, solar cells, touch screens, sensors and biosensors, wearable electronics, and drug delivery systems. As their characteristics depend strongly on their size and morphology, it is essential to find the optimal and most cost-effective synthesis method with precise control over the size and morphology of the wires. Various methods for AgNW synthesis have been reported along with process optimization and novel techniques to increase the yield and aspect ratios of synthesized AgNWs. The most promising processes for synthesis of AgNWs are wet chemical techniques, in which the polyol process is low cost and simple and provides high yield compared to other chemical methods. Reaction mechanism is one of the most important factors in strategies to control the process. Our purpose here is to provide an overview on the main findings regarding synthesis, preparation, and characterization of AgNWs. Recent efforts in the polyol synthesis of AgNWs are summarized with respect to product morphology and size, reaction conditions, and characterization techniques. The effect of essential factors such as reagent concentration and preparation, temperature, and reaction atmosphere that control the size, morphology, and yield of synthesized AgNWs is reviewed. Moreover, a review on the novel modified polyol process and reactor design such as continuous millifluidic and flow reactors to increase the yield of synthesized AgNWs on large scales is provided. The most recent proposed growth mechanisms and kinetics behind the polyol process are addressed. Finally, comparatively few available studies in green and sustainable development of 1D silver nanostructures through the application of natural products with inherent growth termination, stabilization, and capping characteristics are reviewed to provide an avenue to natural synthesis pathways to AgNWs. Future directions in both chemical and green synthesis approaches of AgNWs are addressed.

1. Introduction

The transition from the micro to the nanoscale leads to essential changes in the physical and chemical properties of particles because of both quantum effects and the resulting high ratio of the surface area to the volume. Nanowires show specific electrical conduction characteristics due to their quantum directional configuration. This configuration includes two quantum confined directions, as well as one unconfined direction that provides electrical conductivity. Nanowires are exceptional compared to bulk materials because of their electronic state density and high aspect ratio [1–5]. Metal one-dimensional (1D) nanostructures can play a valuable role in several applications and have recently gained much research attention because of their unique electrical, optical, mechanical, thermal, and catalytic properties.

Having the highest bulk electrical and thermal conductivity among metals (6.3 x 10^7 S/m), silver is one of the most promising metal nanowire materials [3, 6–10]. Silver metal has a range of characteristics that can be improved, adjusted, or developed by control of particle morphology on the nanometer scale. Silver has a face-centered-cubic (fcc) structure
with lattice parameters similar to gold [5, 11]. The variety of metal nanoparticles that have been produced illustrate the various biochemical and physiochemical properties that enable novel technologies and devices [12]. Among these, silver nanoparticles (AgNPs) have unique and outstanding shape- and size-dependent electrical, thermal, optical, catalytic, optoelectronic, anticancer, biosensing, medicinal, antiviral, and biological characteristics which make them exceptional for several applications in a variety of fields and disciplines such as dentistry, drug delivery, biomedical, anticancer, antimicrobial, antioxidant, food science, agriculture, cosmetic, clothing, water treatment, larvicides, forensic science, pollution control, waste management, and photovoltaics [12–21]. Silver has an inhibitory activity toward various biochemical and physiochemical properties that metal nanoparticles that have been produced illustrate the with lattice parameters similar to gold [5, 11]. The variety of metal nanoparticles that have been produced illustrate the various biochemical and physiochemical properties that enable novel technologies and devices [12]. Among these, silver nanoparticles (AgNPs) have unique and outstanding shape- and size-dependent electrical, thermal, optical, catalytic, optoelectronic, anticancer, biosensing, medicinal, antiviral, and biological characteristics which make them exceptional for several applications in a variety of fields and disciplines such as dentistry, drug delivery, biomedical, anticancer, antimicrobial, antioxidant, food science, agriculture, cosmetic, clothing, water treatment, larvicides, forensic science, pollution control, waste management, and photovoltaics [12–21]. Silver has an inhibitory activity toward several microorganisms and bacterial strains and can be used in arthroplasty, medicine, and to prevent bacterial colonization [22]. The ionic form of silver (Ag⁺) is an eco-friendly antimicrobial that can be used against several fungal and bacterial pathogens. Moreover, among metal nanoparticles, AgNPs are a promising candidate for Surface Enhanced Raman Scattering (SERS) applications because of their high optical cross section in the visible region [23]. 1D metal nanostructures have several applications that are unattainable with nanospheres [2, 24]. Moreover, by the application of various capping, growing, and shape control agents in metal nanoparticle synthesis, 1D structures such as nanorods, nanotubes, and nanowires can be produced.

Structural and dimensional properties of nanowires, which play an important role in determination of their characteristics, can be probed by several imaging techniques [25, 26]. Due to the nanoscale size, which is comparable to or less than the wavelength of visible light, electron microscopic techniques are required to create images of the particles. These include but are not limited to Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and High-Resolution Transmission Electron Microscopy (HRTEM). Scanning Tunneling Probes (STP) and X-ray analysis may also be used to characterize nanowire [3]. Based on the specific application, other characterization methods may be used to evaluate the electrical, mechanical, rheological, and catalytic characteristics of AgNWs.

There are a broad range of applications of AgNWs in several areas including but not limited to nanoelectronics, sensors, biosensors, catalytic, medical, energy devices, agriculture, and food science. AgNWs can be utilized as conductive filler to formulate conductive inks and create conductive patterns [2, 9, 27–29]. They also may be used to enable sensors and biosensors to detect different chemical and biochemical components [30–32] or as wearable electronic devices as strain, pressure, and human activity sensors [33–36]. Moreover, they may be used to create transparent conductive electrodes for applications such as solar cells, LCDs, LEDs, and touch screens [37–47]. Finally, there are challenges and drawbacks in using the alternative material Indium Tin Oxide (ITO) which is chemically unstable, increasing in cost with a limited supply of indium, and in some applications, forms brittle films. All of these reasons make it necessary to replace ITO, and AgNW has gained attention as a promising material to replace ITO for Transparent Conductor (TC) device fabrication in touch screens, solar cells, and displays [48].

This review article is helpful for new researchers to select the appropriate direction in polyol synthesis of AgNWs with desired size and morphology. Moreover, this article would lead them toward the green and sustainable synthesis of 1D silver nanostructures that have not been reviewed in previous studies.

2. Effect of AgNW Size and Morphology on Material Characteristics

The physical and chemical characteristics of AgNWs such as thermal, electrical, catalytical, optical, mechanical, rheological, and antimicrobial behaviors in different applications are strongly size and morphology dependent. It has been shown that the conductance of metal nanowire such as AgNW is quantized due to their dimension that is comparable to the electron Fermi wavelength that makes them a unique candidate for nanoelectronics [4]. The correlation between electronic characteristics and structural properties of AgNWs has been confirmed by theoretical calculations [5]. The application of AgNWs in transparent conductive electrodes (TCE) due to their size- and morphology-dependent electrical resistance and transmittance for electronic and optoelectronic applications has been proved [10, 27, 29, 33, 49]. Size- and morphology-dependent characteristics of AgNWs make them more potent antibacterial with lower cytotoxicity compared to other silver nanoparticles [21]. AgNW has also been used in sensor and biosensor applications in which its photon-plasmon interaction and electromagnetic scattering characteristics are strongly depend on its size and morphology [30]. In the application of metal nanostructures as catalysts, their selectivity and activity strongly depend on the atomic arrangement and surface crystal plane [50].

Hemmati et al. showed that conductive inks formulated with high aspect ratio AgNW (length of 30 μm and diameter of 40 and 90 nm) content as low as 3 wt.% provide high-quality screen printing with sharp-line definition, which is difficult to achieve with low aspect ratio AgNW, micrometer-sized silver particles, or silver flake at the same content. Based on the viscosity measurements under conditions designed to mimic screen printing, it was shown that the dynamic viscosity of the ink depends strongly on AgNW content. This effect was stronger at higher concentration of AgNWs [2].

These size- and morphology-dependent characteristics of AgNWs point to the necessity to utilize a synthesis process in which size and morphology of the synthesized AgNWs can be precisely controlled with narrow size distribution.

3. Polyol Synthesis and Characterization of AgNWs

There are several methods for AgNW synthesis, which can be broadly categorized as template-free and template-directed methods. The chemistry of AgNW synthesis can
be categorized into vapor phase and liquid phase methods. The latter has been used widely because of the variety of suitable solvents, easy monitoring, low cost, and a homogenous reaction regime [3]. The most promising processes for synthesis of AgNWs are wet chemical techniques. Among these, the polyol technique is a superlative method compared to other chemical methods as it is low cost and simple and provides high yield [6, 7, 9]. Fievet et al. investigated and illustrated the advantages of polyol process compared to other methods for metal nanoparticle synthesis [51]. Size distribution, shape selectivity, and morphology control are the essential challenges in nanomaterial synthesis [52, 53]. It is crucial to control the mean and variance of length and diameter.

Most recently, Fahad et al. provided an overview on AgNW synthesis and their application as conducting material. Their overview on different synthesis methods including photoreduction method, template method, wet chemical method, and solution-based synthesis concluded that the polyol-assisted solution-based method is the dominant one in synthesis of homogeneous high aspect ratio AgNWs. The factors that affect the morphology and size of synthesized AgNWs include mole ratio, capping agent molecular weight and its rate of addition, reaction atmosphere, reaction temperature, reaction time, and stirring rate were reviewed [54]. Zhang et al. reviewed advances in synthetic methods and applications of silver nanostructures. They summarized the preparation of various sizes and morphologies of silver nanostructures including nanospheres, nanocubes, nanowires, and nanorods and provided a summary of reaction conditions for their synthesis [55]. Zhang et al. also provided a review on synthesis, growth mechanism, and multifunctional applications of AgNWs specifically as conductive materials and component of electronic devices. Examples of silver nanostructures include perfect/truncated cube, beam, right bipyramid, rectangular bar, tetrahedron, octahedron, triangular/hexagonal plate, decahedron, rod, and wire. Based on the conventional definition of AgNWs, diameters are in the range of 10-200 nm and lengths in the range of 5-100 μm. Based on this definition, AgNWs have aspect ratios of more than 10 and similar structures with smaller aspect ratio are called nanorods [56].

In this review, we focus on the polyol synthesis which was introduced by Fievet et al. to synthesize submicron-sized metallic nanostructures [57, 58]. A polyol solvent in the presence of a salt precursor and a polymeric capping agent is heated to produce a metal colloid. In the case of AgNWs, ethylene glycol (EG), silver nitrate (AgNO₃), and poly(vinyl pyrrolidone) (PVP) usually function as the polyol, salt precursor, and capping agent, respectively. The synthesis process is chemical reduction of Ag ions in the presence of a polymeric capping agent, in which a small amount of suitable salt can facilitate the growth of the silver seeds to the wire shape [9]. Several factors affect the morphology and yield of AgNWs, including reagent concentration, rate of reagent addition, preparation of the silver ion solution, capping agent molecular weight, type of salt, type and power of stirring, reactor volume in batch synthesis, and residence time in flow synthesis [59–69].

Because of their influence on material properties, the size and morphology of nanowires, including their shape and crystal structure, must be accurately guided during synthesis. As the nanoparticle size can be studied and monitored by UV-visible absorption spectroscopy, this technique plays an essential role in investigations of the nanoparticle synthesis reaction mechanism. In situ UV-vis characterization can also be used to investigate the kinetics of the reaction [70] or to monitor the extent of reaction [71]. In the case of silver nanowires (AgNWs), a broad peak around 400 nm is due to transverse plasmon absorbance, while a shoulder peak around 350 nm is due to the plasmon resonance of bulk silver [8, 72, 73]. The full width at half maximum (FWHM) can be used to determine quantitatively the size and size distribution of the synthesized metal nanostructures [74]. Fourier Transfer Infrared (FTIR) is used to identify functional groups from the position of the peaks in the spectrum [19, 75]. With FTIR analysis, it is also possible to identify metabolites such as amine, ketone, alcohol, aldehyde, carboxylate, or other functional groups attached to the nanowires [76, 77]. Structure changes on the surface of nanoparticles can be investigated by X-ray Photoelectron Spectroscopy (XPS) [78]. Small Angle X-ray Scattering (SAXS) can provide a precise and statistically feasible way to investigate the uniformity of metal nanoparticles and their size distribution [79]. Electron microscopy methods such as TEM, HRTEM, and SEM are used to investigate the morphology of the synthesized nanostructures and their size or the morphology of the different structures ex situ. In situ X-ray adsorption spectroscopy (XAS) is a versatile technique that permits investigation of the reaction dynamics and mechanism of AgNW growth by observation of oxidation state changes, time-resolved bond formation, coordination, and local order.

Xia’s group has published several studies of AgNW synthesis relevant to our subject [80, 81]. In one of these, Sun et al. described a polyol process in which platinum nanoparticles act as seeds for heterogeneous nucleation and growth of silver particles in the presence of PVP to produce AgNWs. In another study, they used seed-assisted solution-based polyol AgNW synthesis and investigated the effect of reagent addition procedures on the yield and morphology [82, 83]. In another study by this group, Wiley et al. investigated the polyol synthesis of Ag nanostructures including cuboctahedra, pentagonal, nanowires, bipyramids, nanocubes, nanobars, and nanobeams with controlled properties and shape [11]. Skrabalak et al. investigated glycolaldehyde (GA) as a reducing agent in polyol synthesis of Ag nanostructures. By a spectrophotometric method, they showed that heating EG in air results in its oxidation to GA, which acts as a reductant for noble metal ions such as silver [84]. In a recent study, Luo et al. introduced the facile synthesis of Ag nanorods in the presence of palladium nanostructures (decahedra of 16 nm) as seeds to direct the nucleation, deposition, and growth of the Ag atoms into a 5-fold twinning axis to facilitate the growth to the wire shape. In this mechanism, the diameter of the Ag nanorods depends on the lateral dimensions of the seed. In their process, poly(diallyldimethylammonium chloride) (PDDA) functions as both an anion provider and
a cation provider and as a capping agent to facilitate growth of nanorods [85].

Korte et al. investigated the rapid synthesis of AgNWs in the presence of PVP as a stabilizer and CuCl or CuCl₂ as a salt mediator. They showed that both Cl⁻ and Cu²⁺, which is a product of the reduction of Cu²⁺ by EG, are necessary for AgNW growth. Cl⁻ is responsible for stabilization of silver seeds by binding silver ions as AgCl and releasing Ag⁺ slowly to prevent supersaturation in the beginning of the reaction. Cu⁺ serves to adsorb atomic oxygen from the surface of silver seeds and facilitates further growth to the wire shape [6].

Based on these studies and other studies regarding the effect of synthesis conditions on the morphology and formation of silver nanowires in the polyl process [86], it is clear that essential factors include reagent concentrations, salt mediator type and concentration, capping agent concentration and molecular weight, reagent solution preparation condition, and reaction temperature that predominantly affect and control the polyl synthesis of AgNWs.

3.1. Effect of Temperature in the Polyl Synthesis of AgNWs. Temperature is one of the essential factors in the polyl synthesis of AgNWs. A high temperature (110-200°C) is required at the beginning of the reaction to generate a reducing agent and to reduce the silver ions to silver atoms.

There are some studies that have investigated the effect of the reaction temperature on the morphology and yield of AgNWs or introduced new heating methods or processes. Coskun et al. investigated the effect of temperature on the length and diameter of AgNWs. They found that the conversion of EG to GA occurs at high temperature and a critical temperature (130-150°C) is required for the formation of a high aspect ratio of AgNWs. Subsequently, the growth of AgNWs is based on the formation of the multiwinned particles at that temperature [87]. Jiu et al. showed that a high temperature is necessary to promote AgCl solubility, while too high temperature produces an undesirably high ratio of the etching rate to the nucleation rate [88]. Lai et al. showed that a reaction temperature in the range of 130-175°C affects the morphology of Ag nanostructures (particles, rods, cubes, and wires) corresponding to different surface plasmon resonance (SPR) properties [89]. Kaili et al. emphasized the importance of temperature in the range of 110-160°C as it determines the diffusion and reaction (nucleation and growth) rates. They showed that nanowire size decreases as the temperature increases due to increasing nucleation and growth [90]. Nghia et al. used a microwave technique (800 W microwave oven equipped with a condenser) to synthesize AgNWs quickly with an irradiation time of 3.5 minutes and found that morphology depends strongly on the rate of heat [59]. Liu et al. also utilized a microwave-assisted (400 W microwave oven with an irradiation time of 3 minutes) to control morphology [91]. Lim et al. reported high yield synthesis of AgNWs by a heated-up (heating from room temperature to desired one at a specific heating rate) polyl process. They observed that the heat-up method can facilitate the formation of seeds and their growth to the wire structure rather than the hot injection polyl method [92].

3.2. Effect of AgNO₃ Concentration, Its Preparation, and Injection Rate in the Polyl Synthesis of AgNWs. Silver nitrate (AgNO₃) usually functions as a metal precursor in AgNW polyl synthesis. Its concentration, preparation method, and the rate of injection are among the most important parameters in the process. At low AgNO₃, the resulting nanostructures consist mainly of particles, spheres, triangle bipyramids, and cubes. With increasing AgNO₃ concentration, the yield of AgNWs compared to other structures increases up to a limit. When AgNO₃ concentration is too high (0.188 M), again there are other nanostructures rather than 1D nanostructures because of the resulting high concentration of seeds early in the process. The injection rate is also crucial as it is important to not have supersaturation of Ag at the beginning of the reaction. This can be achieved either by adding the AgNO₃ solution dropwise or by using a salt mediator that can form the corresponding Ag-based salt (AgM in which M can be different anions such as Cl⁻) and consequently release the Ag ions slowly. Finally, sonication time of the AgNO₃ solution is also essential as it affects the size of the particles that formed as sonication continues.

Nghia et al. investigated the effect of AgNO₃ concentration (15-90 mM) on the morphology and yield of synthesized AgNWs in a microwave-assisted polyl process. They reported the formation of cubes and bipyramids at low concentration and 89% yield of AgNWs at high concentration [59]. Lim et al. investigated the effect of AgNO₃ concentration, and their results showed that the concentration and injection rate of AgNO₃ and the reaction temperature have a strong effect on the growth characteristics of AgNWs. They found that AgNW diameter decreases with increasing AgNO₃ concentration and consequently the wire aspect ratio increases [92]. Wu et al. synthesized AgNWs in a one-pot method without chloride ion. They varied the reagent concentration and injection rate of AgNO₃ and PVP to produce AgNWs with different lengths and widths [93]. Gebeyehu et al. varied and adjusted the concentration of the AgNO₃ (20.6, 30.5, 60.4, and 90.3 mM) and molar ration of [PVP]/[AgNO₃] concentration to control wire morphology. They synthesized AgNWs with aspect ratios of more than 1000 and average diameter of 20 nm by adding 30.5 mM of AgNO₃ and [PVP]/[AgNO₃] of 6:1, followed by 2-3 cycles selective precipitation to purify AgNWs and separate all of other nanoparticles that had produced as a byproduct [94]. Srivastava et al. investigated the effect of AgNO₃ concentration on the nanostructure morphology and size for highly sensitive SERS sensors. They showed that nanowires can be synthesized at lower concentration of AgNO₃ whereas higher concentration caused formation of nanocubes [95].

Lee et al. found that the sonication time of the AgNO₃ solution is important to produce high yield and high aspect ratio AgNWs. They reported that the optimum sonication time is 7 minutes [7].

The injection rate of reagent solutions specifically AgNO₃ solution is essential and can control wire yield and morphology. Coskun et al. showed that the injection rate (1, 3, 5, 6, 8,
and 300 mL/h) affects the morphology and yield of synthesized AgNWs as there were micrometer-sized Ag particles as well as AgNWs at very low or very high injection rates [87]. Amirjani et al. investigated the effect of the rate of AgNO₃ addition on the aspect ratio through a response surface method (RSM). Their statistical results showed that the first order of this parameter and Cl⁻ concentration has a similar effect on the AgNW aspect ratio and their integration is statistically significant. They found the optimum value of <0.047 mmol/min AgNO₃ addition to synthesize uniform AgNWs [96].

3.3. Effect of PVP Concentration and Molecular Weight as a Capping Agent in the Polyal Synthesis of AgNWs. PVP usually functions as a capping agent in the polyol synthesis of AgNWs to stabilize and control the growth of the silver multilayered seeds to 1D nanostructures. PVP molecular weight is an essential factor in the strength of interaction between PVP and silver seeds, and it strongly affects the morphology of the nanostructures. There are several studies aimed at investigating the effect of PVP concentration and molecular weight or the PVP/AgNO₃ ratio.

Sonntag et al. showed the necessity to use a minimum PVP chain length to synthesize AgNWs. They concluded that at their reaction condition the minimum MW of 55 kDa is required to synthesize AgNWs with a small diameter distribution [97]. Coskun et al. showed that the PVP:AgNO₃ molar ratios (3:1, 4.5:1, 6:1, 7.5:1, 9:1, and 11:1) affect strongly the final morphology of the silver nanostructures. They showed that, at very low molar ratio, passivation the {100} faces are incomplete and, by increasing the ratio, the AgNW diameter can be decreased gradually. At a very high molar ratio, there are some micron-sized Ag particles attributed to excess PVP coverage on all faces of the silver seeds rather than selective coverage of {100} faces. They reported an optimum value of 7.5:1 [87]. Song et al. investigated the effect of PVP molecular weight (MW = 8,000, 29,000, 40,000, and 1,300,000) on the morphology and shape of Ag nanostructures. They proposed that adsorption and steric effects are responsible for the effect of PVP on morphology. They suggested that when the PVP MW is low, selective adsorption of PVP on {100} facets is dominant, whereas at higher MW chemical adsorption is distributed on all facets. They also concluded that the MW of PVP is more critical than its concentration [60]. Lim et al. demonstrated that AgNWs with a high aspect ratio can be produced with a PVP/AgNO₃ concentration mole ratio of 16 [92]. Zhu et al. utilized PVP as a capping agent with various MWS (15,000-80,000) and subsequently introduced long-chain PVP to improve the process [98]. Lee et al. showed that AgNW diameter can be controlled by varying PVP concentration [99]. Yang et al. synthesized AgNWs by a modified polyol process in the PVP concentration range of 4.53-13.75 wt.% to produce AgNWs embedded in PVP fibers [100]. Chen et al. synthesized nano-Ag/PVP composites, and the effect of main parameters such as degree of the polymerization of PVP was investigated. They showed that PVP as a capping agent improves the performance of nanosilver dispersion in several solvents due to its great solvent adaptability [74]. Kaili et al. showed that PVP as a capping agent not only plays an essential role in preventing seed agglomeration but also helps heterogeneous growth of MTPs to wire shape. They investigated the effect of PVP molecular weight (55,000, 360,000, and 13,000,000) on the diameter and length of synthesized AgNWs and showed that while PVPs with large MW provide better product quality, very large MW (13,000,000) PVP is not suitable for synthesis of AgNWs with a high aspect ratio without nanoparticles as byproducts due to the viscous effect of the polymers [90].

3.4. Effect of the Salt Mediator in the Polyal Synthesis of AgNWs. In the polyal process, a small amount of a suitable salt is necessary to assist growth of silver nuclei to wire shape. The required anion and cation can be provided by several types of salts such as CuCl₂, CuCl, NaCl, FeCl₃, NaBr, KBr, and CrCl₃. Several studies have investigated the effect of the salt type and its concentration on morphology and yield.

Zhang et al. conducted polyl AgNW synthesis in the presence of several metal ions including NaCl, CoCl₂, FeCl₃, and CrCl₃ with concentration of 86 μM to investigate their influence on morphology and yield of synthesized AgNWs. They concluded that the Cr³⁺ as a novel and promising metal ion in polyl AgNW synthesis not only can scavenge the atomic oxygen and prevent oxidative etching but also provides a more stable reaction environment when coupled with hydrothermal synthesis. AgNWs with lengths of up to 160 μm and yield of more than 90% were reported [101]. Yuan et al. used tetrabutylammonium dibromochloride (TBADBC) as organic auxiliary in an AgNW polyl process to synthesize AgNWs with diameters as small as 16 nm with aspect ratios over 2000. They attributed this result to passivation by AgClBr₂ particles on the {100} crystal facet of the initially formed Ag pentahedral seeds [102]. Chen et al. investigated how the diameter of AgNWs could be adjusted by introducing specific control agents, including metal cations, inorganic anions, and molecules such as KBr, KOH, KCl, Fe(NO₃)₃, PdCl₂, Na₂S, and ascorbic acid [103]. Nghia et al. introduced NaCl as a salt mediator to control the silver reduction rate and initial seed formation in a microwave-assisted polyl process. They showed that in the absence of NaCl, AgNP formation is dominant (around 96%) [59]. Jiu et al. explained how a trace amount of suitable salt including FeCl₃, NaCl, or Na₂CO₃ is necessary for AgNW growth because of the formation and dissolution of Ag₂Cl₂ between Ag ions and anion in salt [88]. Coskun et al. investigated the effect of NaCl concentration (0, 8.5, 12, 17.1, 25.6, and 85.5 μM) and showed that in the absence of Cl⁻ ions there are only silver nanoparticles (AgNPs) due to the rapid reduction of Ag⁺ to Ag⁰. Addition of NaCl facilitates the formation of the AgNWs due to the formation of AgCl and slows the release of the Ag ions [87]. Zhang et al. synthesized single-crystal AgNWs with smooth surfaces through a sulfide-mediated polyl process by utilizing Na₂S as a salt mediator [30]. Liu et al. utilized a (NH₄)₂CO₃-mediated polyl process instead of a conventional salt-mediated polyl process to improve metal purity and showed that the resulting AgNWs had rounded ends instead of [111] crystal planes [104]. Johan et al. proposed a growth mechanism based on various
mediating agents such as CuCl₂ and NaCl. They concluded that the presence of both cation and anion is necessary for the formation of AgNWs and showed that in the absence of mediating agents the final products include particles as well as wires [62]. Amirjani et al. investigated the effect of the Cl⁻ concentration in a CuCl₂-mediated polyol process on aspect ratio of AgNWs, and they found an optimum value of <2 mM Cl⁻ to produce uniform AgNWs [96]. Schuette et al. utilized NaCl as a salt mediator and showed that it is responsible for AgCl nanocube formation with different sizes as heterogeneous nucleants for subsequent wire growth. As the AgNW diameter was almost independent of AgCl size, they showed that the nucleation event had little influence on the AgNW diameter. Their kinetic investigation showed that the AgNW length, diameter, and aspect ratio grow in parallel and consequently proved that growth is limited by the rate of reduction through a surface-catalyzed reduction in which Ostwald ripening or aggregation of NPs is essential component of the growth mechanism [105]. Li et al. utilized a polyol process not only to synthesize AgNWs but also to control their diameter and consequently their optoelectronic properties through addition of bromide (NaBr) [106]. Lee et al. utilized a polyol process in the presence of propylene glycol (PG) as a solvent and a reducing agent, PVP as a capping agent, and 1-butyl-3-methylimidazolium chloride (BMIM-Cl) as a growth controller. They showed that AgNW length can be adjusted by changing the PVP/BMIM-Cl concentration ratio [99]. Zhang et al. introduced a new one-pot polyol synthesis by using KBr as a capping agent (NaCl, which is advantageous for AgNW reduction size [107]. Silva et al. introduced a method for the facile synthesis of AgNWs by using both PVP and Br⁻ ion as a capping agent. They showed that the ratio of PVP to Br⁻ ions controls the reduction kinetics and can be used to form Ag seeds with decahedral shape and consequently facilitate growth in the desired direction [108]. Zhu et al. investigated the importance of several cations and anions such as Fe³⁺, Cu²⁺, K⁺, Na⁺, H⁺, SO₄²⁻, NO₃⁻, and Cl⁻ as control agents in the polyol synthesis of AgNWs. They explained these effects by slow release of Ag⁺, decrease of the surface oxidation etching phenomenon due to the presence of cations, and low solubility of products due to the presence of anions [65]. Wang et al. investigated the effect of Cu²⁺ ion concentration to rapidly produce long AgNWs. They showed that AgNWs are longer at higher Cu²⁺ concentration [66]. Wang et al. also investigated the effect of chloride ions to produce very long AgNWs in a rapid process. They attributed this rapid (~40 min) polyol synthesis to the presence of a high concentration of Cl⁻ that facilitates the production of multilayered Ag seeds during nucleation [67]. Abbasi et al. tried cobalt chloride (CoCl₂) as a salt mediator or growth-promoting additive in the presence of an optimum ratio of glycerol/water (G/W) as a solvent to synthesize AgNWs not only rapidly but with morphology control as well [109]. Satoungar et al. investigated the effect of several mediation agents (FeCl₃, FeCl₂, and AlCl₃) on the morphology of AgNWs through the use of 1,2-propanediol and EG as a solvent and a reducing agent. They showed that Cl⁻ ions are responsible for electrostatic stabilization and AgCl colloid formation in the initial stage of silver seed formation [68]. Liu et al. utilized a microwave-assisted (400 W for 3 min) polyol method to control nanostructure morphology by varying the Na₂S concentration with all other reaction parameters held constant. They found a spherical-cube-linear morphology progression as the concentration of Na₂S was increased [91]. Zhao et al. regulated the morphology and size of AgNWs with ferric chloride (FeCl₃) as a mediation and nucleation agent and PVP as a capping agent to synthesize AgNWs with aspect ratio up to 570 (from 250 to 570) [110]. Rui et al. investigated the effect of Cl⁻ and Br⁻ in the polyol synthesis of high yield (>85%) and high aspect ratio (up to 2500) of AgNWs. They used the electron trap distribution (ETD) of the silver halide crystals to investigate the simultaneous effect of Cl⁻ and Br⁻ ions in the synthesis of high aspect ratio AgNWs of small diameter by providing uniform EDT through formation of silver halide AgBr₁₋₃Cl₂ [111]. Bobinger et al. tailored the various polyol parameters such as the temperature, PVP to the AgNO₃ ratio, rate of stirring, and type of PVP to synthesize AgNWs with an aspect ratio of 800. They found that a small amount of KCl can reduce the AgNW diameter as well as increase dispersion and stability. They demonstrated the role of KCl as a cocapping agent in the presence of PVP [112]. Trung et al. also illustrated the necessity of a suitable mixture of metal salts. They showed that the diameter of the AgNWs can be decreased and their length increased by an increase in the NaCl concentration. They also showed that the addition of NaBr at an appropriate ratio can further decrease the diameter of the synthesized AgNWs [113]. Lei et al. controlled the diameter and length of AgNWs by varying the concentration of KBr and MnCl₂. A kinetic investigation (reaction rate and reaction activation energy) of the Ag ion conversion to Ag atoms proved that their introduction to the process plays an essential role in producing very long AgNWs with a high aspect ratio [114].

3.5. Effect of the Mixing Type and Rate in the Polyol Synthesis of AgNWs. Provision of a high, uniform, and consistent rate of mass and heat transfer is required in the polyol synthesis particularly when the synthesis is carried out on a large scale. This can be achieved by efficient mixing to generate seeds, nanoparticles, and consequently nanowires in sufficient quantity. There are some studies that investigated the effect of the rate and power of stirring on nanowire morphology.

Coskun et al. investigated the effect of the stirring rate (10-1000 rpm) along with the effects of other reaction parameters on product morphology to optimize reaction conditions. They observed formation of AgNWs at all stirring rates and even in stagnant solution. In stagnant solution, they observed formation of micron-sized particles as well as large-diameter nanowires [87]. Andres et al. reported a rapid (less than 1 hr) one-pot polyol synthesis process to produce very long AgNWs by adjusting the temperature and stirring rate [115]. Amirjani et al. in another study also investigated the effect of the agitation rate on the polyol synthesis of AgNWs. They showed that by increasing the agitation rate, oxidation etching would be enhanced leading to formation of various nanostructures such as nanoparticles, nanorods, and nanowires. They illustrated that agitation is not necessary for AgNW synthesis, but the AgNW diameter can be decreased.
by setting the stirring rate at 200 rpm [116]. Junaidi et al. investigated the effect of the rate of stirring on AgNW polyol synthesis using polyvinyl alcohol (PVA) as a capping agent and a stabilizer without adding any salt mediator. They showed that optimal formation of AgNWs would be achieved at 350 rpm [69].

3.6. Modified Polyol Processes. There are also some studies that investigated modified polyol processes such as the successive multistep growth method (SGM), novel solvents or cosolvents, novel capping agents, or novel reaction conditions such as high pressure.

Lu et al. proposed a modified multistep polyol process including two AgNO₃ additions corresponding to two extents of conversion of the silver precursor into MTPs as well as the NW growth step. They also utilized a novel separating reagent (formamide) to remove the organic solvent and extra surfactant on the surface of synthesized AgNWs [117]. Fahhad et al. carried out the polyol AgNW synthesis process in a salt-free environment and Argon atmosphere. Their process included five steps: EG preheating for 20 minutes, Argon gas flushing for 1 minutes, AgNO₃ injection within 5 minutes, PVP injection within 10 minutes, and reaction mixture heating for 2 hours. They reported that the most important factors controlling the morphology and yield of AgNWs are the reaction temperature and AgNO₃/PVP ratio [118]. Liu et al. reported a modified polyol process for AgNW synthesis with sharp end by controlling the AgNW growth, oxidative etching, and PVP passivation rates occurring at the tip of AgNW for scanning tunneling microscopy and tip-enhanced Raman spectroscopy applications [119]. Inose et al. also used a water-mediated polyol process to synthesize pencil-like sharp AgNWs by adding an appropriate amount of pure water (0.2–0.4 (v/v), %) in the conventional polyol synthesis [120]. Wang et al. introduced AgCl particles (reaction products between NaCl and AgNO₃) as seeds for heterogeneous nucleation in a modified polyol process. The amount and reaction time of AgCl as well as reaction temperature were adjusted to synthesize uniform AgNWs with small diameters of about 52 nm and aspect ratios above 1000 [121]. Li et al. introduced a modified fast (30 minutes) polyol synthesis process by finding the optimum conditions to synthesize AgNWs with diameters of 53 ± 9 nm, lengths of 31 ± 7 μm, and aspect ratio of 584.9 [122]. Andrew et al. introduced a solution-based low temperature method to synthesize AgNWs and to functionalize their surfaces by either displacement or adsorption. They showed that the adsorption of a luminescent polymer or PVP thiol displacement can be used to functionalize AgNWs. Characterization demonstrated polymer inhomogeneity on the AgNW surfaces and noninteracting polymer excitons [123]. Lee et al. introduced a successive multiple growth (SMG) polyol process in which AgNWs produced in a first synthesis are used as seeds to grow very long AgNWs. They showed that this process can be repeated up to seven times to produce extremely high aspect ratio (1000–3000) AgNWs [7]. Jiu et al. utilized a salt-assisted hydrothermal process to synthesize AgNWs by using PVP not only as a polymeric capping agent but also as a reducing agent in deionized water (DIW) in an autoclave [88]. Hua et al. introduced a successive multistep process to produce ultrathick AgNWs. This was achieved through the initial formation of thin AgNWs as seeds for growth of thick AgNWs [124]. Yang et al. reported a water-involved synthesis of AgNWs by a rapid and scalable heterogeneous nucleation process. They proposed that the addition of small amounts of water with an optimal ratio to the reducing agent of 0.25% plays an essential role in obtaining a high yield of AgNWs [73]. Zhao et al. reported a water-assisted polyol process to increase the aspect ratio of AgNWs and demonstrated the effect of a proper amount of water in promoting and facilitating the charge transfer process as transfer of electrons are easier in polar solvents [125]. Lee et al. utilized a polyol process in the presence of propylene glycol (PG) as a solvent and a reducing agent, PVP as a capping agent, and 1-butyl-3-methylimidazolium chloride (BMIM-Cl) as a growth controller [96]. Moon et al. synthesized AgNWs with glycerol/DIW as a solvent and a reducing agent in a polyol process [126]. Lee et al. reported the synthesis of ultrathin AgNWs with a high aspect ratio around 1000 by a polyol process under high pressure reaction conditions. They showed that high pressure can enhance the rate of nucleation and consequently decrease the AgNW diameter [127]. Abbasi et al. tried cobalt chloride (CoCl₂) as a salt mediator or growth-promoting additive in the presence of an optimum ratio of glycerol/water (G/W) as a solvent to synthesize AgNWs at high rates with good morphology control [109]. Junaidi et al. introduced a polyol synthesis using polyvinyl alcohol (PVA) as a capping agent and a stabilizer without adding any salt mediator [69]. Patarroyo et al. introduced a novel high yield green silver nanorod (AgNR) synthesis in the presence of tannic acid as an assistance to nucleate decahedral seeds needed for the monodisperse AgNP production [128].

Recently, Liu et al. also introduced the use of glycerol as a more stable and stronger solvent and a reducing agent containing three hydroxyl groups compared to EG for synthesis of thin and uniform AgNWs. Glycerol can be heated to a higher temperature due to its higher boiling point of 290°C compared to the EG boiling point of 197°C. They synthesized AgNWs up to 10–20 μm in length and 40–50 nm in diameter without addition of salt mediators, chlorides, and template salts by autoclaving mixtures at 197°C for 9 hr. The autoclave step prevents the oxidation of glycerol in air and consequently formation of acrolein and light-yellow polymer [129]. Li et al. synthesized AgNWs as long as 160 μm with 40–85 nm diameter with glycerol as a solvent and a reducing agent and heating at 150°C [130]. Jang et al. synthesized AgNWs as long as 65 μm with an aspect ratio up to 1500 in a tetrabutylammonium dichlorobromide (TBADCB) salt-based polyol synthesis process in which the wire diameter can be controlled by the TBADCB/AgNO₃ molar ratio and length can be controlled by mechanical stirring (unidirectional axial stirring) and reaction temperature. In this process, TBADCB, an organic halide with high thermal stability, acted as a soft template and ionic halogen salt containing an ammonium cation and a BrCl₂⁻ anion [131]. Wei et al. introduced a facile polyol synthesis of segmented
AgNWs through end-to-end self-connection of twinned crystals of neighboring rods or wires with an average diameter of 66 nm [132]. Tang et al. studied a novel modified AgNW synthesis process to control and reduce the high activity defects of synthesized AgNWs through an etching process in which a locally uneven ligand distribution is required to provide more ligand molecules in the nucleation step and less in the growth step. They showed that the AgNWs synthesized in this etching process have fewer straight defects with similar morphology to pentatwinned structures compared to the AgNWs synthesized via a nonetching route [133]. Xi et al. recently used ethylene glycol (EG) and diethylene glycol (DG) as the combined solvents and reducing agent to synthesize ultrathin AgNWs in a large-scale polyol process. They showed that adjustment of the ratio between these two solvents and reducing agents can control their reduction activity and viscosity. They produced AgNWs with 100 nm diameters in the presence of EG and decreased the diameter to ~35 nm using a EG/DG ratio of 4/1 to 3/2 [134]. Rekha et al. recently reported the synthesis of silver nanorods (AgNRs) by a modified seed-mediated method at room temperature [135]. Ni et al. used a modified polyol process with the addition of benzoin to synthesize AgNW with diameters as small as 13 nm and aspect ratios of up to 3000. They also controlled the temperature in the course of the reaction by forming AgCl and AgBr at room temperature and then increasing the temperature to 150°C or 160°C, depending on the desired diameter, while controlling the stirring rate [136]. Zhabg et al. used a polyol process with high molecular weight PVP and FeCl₃ as a capping agent and a salt mediator, respectively, to produce a high aspect ratio (length up to 220 μm) of AgNWs at relatively low temperature (130°C) and long reaction time (8 hr). For the first time, they used filter cloths for purification and to separate short nanowires, AgNRs, and AgNPs produced as byproducts [137]. Chen et al. devised a modified polyol process using both stirred and stagnant conditions during the synthesis process and combined that with a heating process. They increased the temperature over 15-20 minutes up to 180°C while purging the reaction solution with Nitrogen. This was followed by 10 minutes at temperature of 170°C while stirring but without Nitrogen purging. After 10 minutes of stirring, the reaction was brought to completion after one hour at the stagnant condition to produce AgNW with diameters of about 21 nm and lengths of up to about 20 μm. They also introduced a novel water-based purification method along with a small amount (5 ppm) of surfactant such as fluorocarbon surfactant as the purifying agent [138]. Yi et al. used a microwave-assisted technique in the presence of NaBr to control the morphology and size of the synthesized nanostructures as well as to reduce the reaction time from hours to minutes by controlling the NaBr concentration, and microwave time and power that can provide different reaction energies and consequently different reaction rates [139]. Xu et al. utilized a modified polyol process to synthesize very long AgNW (~220 μm) by mixing two different molecular weights (58,000 and 360,000) of PVP as a capping agent. The solution was prepared at room temperature and transferred to a heat transfer bath at 130°C. The solution was first stirred just 10 minutes and then left unstirred for 3.5 hr [49]. Sim et al. introduced the formation of AgNWs without addition of an organic capping agent and a stabilizer such as PVP by using small amounts of NaCl and Fe(NO₃)₃ at a low temperature of 110°C for a long reaction time of 15 hr without stirring [140].

In a study by Hemmati et al., the polyol process based on the method introduced by Xia’s research group was used [6]. The reactor volume was scaled up twenty times for application to conductive inks adaptable for the screen printing process [9]. They performed a parametric study on the polyol synthesis of AgNWs to find the most important parameters that control the yield of AgNWs compared to other Ag nanostructures. They investigated the effect of several parameters such as temperature, reagent concentration, PVP MW, rate of stirring, and sonication time for AgNO₃ solution preparation. Based on this parametric study, it was found that four parameters (temperature, AgNO₃ concentration, PVP concentration, and CuCl₂ concentration) are the most important factors affecting AgNW yield (percentage of AgNWs in respect to other Ag nanostructures). A design of experiment (DoE) procedure was used to investigate the simultaneous effect of these parameters on the AgNW yield and to optimize synthesis to maximize AgNW yield [141].

Table 1 shows a summary of the reaction conditions such as reaction time and temperature, reagent precursor, additive and salt mediator, reducing agent, morphology and dimensions of the Ag nanostructures, and the characterization techniques used in several studies of the polyol synthesis of AgNWs.

3.7. Polyol Flow and Continuous Synthesis of AgNWs. There are a few studies regarding the polyol synthesis of AgNWs in flow reactors to achieve better control of morphology and to scale up the process with high quality, high yield, and high aspect ratio relative to batch reactors. Gottesman et al. utilized a millifluidic reactor to synthesize AgNWs at high yield (92%) by optimizing the reaction conditions at an elevated temperature of 198°C close to the solvent (EG) boiling point and in the absence of any salt mediator. They found that the best morphology can be obtained at 30 min reaction time with a nanowire length in the range of 2-50 μm and average length of ~10 μm and diameter of 71 nm ± 2 [143]. Espinosa et al. synthesized five grams of AgNW using both batch and flow methods. They utilized a 1/4-inch stainless steel tube reactor equipped with the HPLC pump for the flow synthesis of AgNW using EG, AgNO₃, PVP, and CuCl₂ as the solvent and reducing agent, silver precursor, capping agent, and salt mediator, respectively, at temperature of 152°C. They reported flow synthesis of AgNW with lengths of 10-20 μm and thicknesses of 50-100 nm [64]. Yun et al. utilized a trapped tubular flow reactor for polyol AgNW synthesis by using EG, PVP/sodium dodecyl sulfate (SDS), AgNO₃, and NaBr as the solvent and reducing agent, capping agent, Ag precursor, and seeding agent, respectively, at temperature of 160°C. They suggested that high-yield AgNW synthesis without defects can be attributed to the absence of excessive shearing that happens in a stirred batch reactor. They reported the synthesis of AgNW with the length of 30-80 μm and diameter of 80 nm [144]. Lau et al.
| Regent precursor/capping agent | Reducing agent | Salt mediator | Reaction time, temperature/heating | Morphology & dimensions | Characterization techniques | Ref. |
|-------------------------------|---------------|---------------|-----------------------------------|------------------------|---------------------------|-----|
| AgNO$_3$/PVP                 | EG            | NaCl          | 1 hr at 170°C                     | NW                     | Diameter: 26 nm Length: 1113 nm | [142]|
| AgNO$_3$/PVP                 | EG            | —             | 2 hr plus injection time for AgNO$_3$ (5 s) and PVP (10 min) at 160°C | NW                     | Diameter: Average of 56 nm Length: Average of 12 μm | [118]|
| AgNO$_3$/PVP                 | EG            | TBADBC        | 40 min at 25°C (stirring) 2 hr at 25°C (stagnant) 30 min at 120°C Heating at 150/160/170°C | NW                     | Diameter: average of 16 nm Length: average of 35 μm | [102]|
| AgNO$_3$/PVP                 | EG            | NaCl, CoCl$_2$, FeCl$_3$, and CrCl$_3$ | 3 hr at 160°C | NW | Diameter: ~80 nm Length: 75-160 μm | [101]|
| PtCl$_2$, AgNO$_3$/PVP       | EG            | —             | 60 min at 160°C                  | NW                     | Diameter: 30-40 nm Length: ~50 μm | [83]|
| AgNO$_3$/PVP                 | EG            | CuCl, CuCl$_2$, Cu(NO$_3$)$_2$, and NaCl | 60-90 min at 151.1°C | NW | Diameter: 100 nm Length: 10-50 μm | [6]|
| AgNO$_3$, Pd decahedral seeds/PDDA | EG         | —             | 8 hr at 200°C                    | NR                     | Diameter: ~20 nm Length: ~77 nm | [85]|
| AgNO$_3$                     | EG            | KBr, KOH, KCl, Fe(NO$_3$)$_3$, PdCl$_2$, Na$_2$S, and ascorbic acid | 2 hr at 180°C | NW | Diameter: 30-450 nm | [103]|
| AgNO$_3$/PVP                 | EG            | —             | 60 min at 160°C                  | NW                     | Diameter: 60-100 nm Length: 90 μm | [123]|
| AgNO$_3$/PVP                 | EG            | NaCl          | 170°C                            | NW                     | SEM and XRD | [87]|
| AgNO$_3$/PVP (MW: 15,000)    | EG            | —             | 150°C                            | NP (~60%)/NW (~40%) D: ~120 nm L: ~3 μm | FE-SEM, TEM, XRD, UV-vis, and IR spectroscopy | [98]|
| AgNO$_3$/PVP (MW: 38,000)    | EG            | —             |                                  | NP (~50%)/NW (~50%) D: ~100 nm L: ~3 μm | |
| Regent precursor/capping agent | Reducing agent | Salt mediator | Reaction time, temperature/heating | Morphology & dimensions | Characterization techniques | Ref. |
|-------------------------------|----------------|---------------|------------------------------------|-------------------------|-----------------------------|-----|
| AgNO₃/PVP (MW: 58,000)       |                |               | NP (~10%)/NW (90%)                | D: ~180 nm L: ~8 μm     |                             |     |
| AgNO₃/PVP (MW: 200,000)      |                |               | NP (~5%)/NW (~95%)                | D: ~120 nm L: ~8 μm NW (~99%) |                             |     |
| AgNO₃/PVP (MW: 800,000)      |                |               | D: ~100 nm L: ~10 μm              |                         |                             |     |
| AgNO₃/PVP EG                 | EG             | NaCl          | 3.5 min Microwave heating          | NW                      | TEM                         | [59]|
| AgNO₃/PVP EG                 | EG             | CuCl₂         | 90 min 151.1°C                    | NW                      | SEM, HR-TEM, and XRD       | [7] |
| AgNO₃/PVP EG                 | EG             | —             | 60 min 160°C                      | NW                      | FE-SEM, TEM, UV-vis, and XRD | [58]|
| AgNO₃ in PVP in DIW          |                | FeCl₃, NaCl, and Na₂CO₃ | 24 hr 150°C                | NW                      | SEM, XRD, and UV-vis       | [88]|
| AgNO₃/PVP EG                 | EG             | Na₂S          | 150°C                             | NW                      | SEM, HRTEM, SAED, UV-vis, and XRD | [30]|
| AgNO₃/PVP EG                 | EG             | FeCl₃         | 145°C                             | NW                      | TEM, XRD, and UV-vis       | [89]|
| AgNO₃/PVP EG                 | EG             | (NH₄)₂CO₃     | 60 min 160°C                      | NW                      | SEM, HR-TEM, and SAED      | [27]|
| AgNO₃/PVP EG                 | EG             | FeCl₃         | 151°C (14°C/min)                  | NW                      | SEM, HR-TEM, and UV-vis    | [92]|
| AgNO₃/PVP EG                 | EG             | AgCl          | 170°C                             | NW                      | SEM, TEM, EDS, XRD, and FTIR | [100]|
| Regent precursor/capping agent | Reducing agent | Salt mediator | Reaction time, temperature/heating | Morphology & dimensions | Characterization techniques | Ref. |
|--------------------------------|---------------|---------------|-----------------------------------|------------------------|--------------------------|------|
| AgNO₃/PVP                      | EG            | NaCl          | 1 hr 170°C                         | NW                     | Diameter: 20 nm Length: 20 μm | [106]|
|                                |               | NaBr          |                                   |                        |                          |      |
|                                | Glycerol/DIW  | NaCl          | 210°C (8°C/min)                    | NW                     | Diameter: 60-90 nm Length: 8-12 μm | [73] |
|                                | PG            | BMIM-Cl       | 24 hr 90°C                         | NW                     | Diameter: 45 nm Length: 25 μm | [99] |
|                                | EG            | —             | 30 min 160°C                       | NW                     | Diameter: 100-300 nm Length: 10-50 μm | [93] |
|                                | EG            | NaCl/KBr      | 4 hr 120°C                         | NW                     | Diameter: 26 nm Length: 21 μm | [107]|
|                                | EG            | NaCl and KBr  | 30 min 160-180°C                  | NW                     | Diameter: 200 nm Length: 110 μm NW Diameter: 50 nm Length: 80 μm | [115]|
|                                | EG            | NaBr          | 35 min 160°C                       | NW                     | Diameter: 20 nm Length: 20 μm | [108]|
|                                | EG            | CuSO₄·5H₂O    | 60 min 160°C                       | NW                     | Diameter: 31-57 nm Length: 50 μm | [65] |
|                                |               | Cu(NO₃)₂·3H₂O |                                   |                        |                          |      |
|                                |               | KCl           |                                   |                        |                          |      |
|                                |               | NaCl          |                                   |                        |                          |      |
|                                |               | FeCl₃·6H₂O    |                                   |                        |                          |      |
|                                |               | CuCl₂·2H₂O   |                                   |                        |                          |      |
|                                |               | HCl           |                                   |                        |                          |      |
|                                | EG            | CuCl₂·2H₂O   | 30 min 160°C                       | NW                     | Diameter: 31-57 nm Length: 50 μm | [66] |
| Regent precursor/capping agent | Reducing agent | Salt mediator | Reaction time, temperature/heating | Morphology & dimensions | Characterization techniques | Ref. |
|-------------------------------|----------------|---------------|-------------------------------------|-------------------------|-----------------------------|------|
| AgNO$_3$/PVP                  | EG             | —             | 40 min (3 steps) 160°C              | NW Diam: 1820 nm L: 40 μm | SEM                         | [124]|
|                               |                | CuCl$_2$      | 40 min 160°C                       | NW Diam: 60-141 nm L: average of 102 and longest of 268 μm | SEM and XRD                  | [67] |
| AgNO$_3$/PVP                  | Glycerol/DIW   | NaCl          | 45 min                              | NW Diam: 45 nm L: 200 μm | SEM                         | [126]|
|                               | EG             | NaCl/KBr      | 1 hr 160°C/(1000 psi (69 bar) of N$_2$) | NW Diam: 16-22 nm L: 20 μm | TEM and SEM                  | [127]|
| AgNO$_3$/PVP                  | G/W            | CoCl$_2$·6H$_2$O | 40 min 160°C                      | NW Diam: 196 nm L: 12.46 μm | TEM, SEM, XRD, and XPS      | [109]|
| AgNO$_3$/PVP                  | 1,2-propanediol and EG | —           | 90 min, 170°C                        | $D = 64$ nm, $L = 12$ μm | TEM, FESEM, XRD, and UV-vis | [68] |
|                               |                | FeCl$_2$      | 60 min, 155°C                       | $D = 88$ nm, $L = 12$ μm |                            |      |
|                               |                | AlCl$_3$      | 120 min, 180°C                      | $D = 180$-230 nm, $L = 20$ μm |                            |      |
|                               |                | FeCl$_3$      | 30 min, 170°C                       | $D = 40$-60 nm, $L = 7$-10 μm |                            |      |
| AgNO$_3$/PVA                  | EG             | —             | 90 min                              | NW Diam: 190 ± 40 nm L: 70 ± 20 μm | SEM, XRD, and UV-vis        | [69] |
| AgNO$_3$/PVP                  | EG             | —             | 1 hr 160°C                          | NW Diam: 40 nm L: 10 μm     | SEM and UV-vis              | [74] |
| AgNO$_3$/PVP                  | EG             | CuCl$_2$      | 90 min 150°C                        | NW Diam: 102 nm L: 3.2 μm   | SEM                         | [9]  |
| Regent precursor/capping agent | Reducing agent | Salt mediator | Reaction time, temperature/heating | Morphology & dimensions | Characterization techniques | Ref. |
|--------------------------------|---------------|---------------|-----------------------------------|-------------------------|-----------------------------|------|
| AgNO₃/PVP                      | Glycerol      | —             | 9 hr 150°C (autoclave)            | NW                      | SEM, XRD, TEM, and UV-vis   | [129]|
| AgNO₃/PVP                      | EG            | NaCl and KBr  | 3 hr 160°C                        | NW                      | FED-SEM, AFM, TEM, EDS, EDX, XRD, XPS, and UV-vis-NIR | [94]|
| AgNO₃/PVP                      | Glycerol      | NaCl          | 5 hr 150°C                        | NW                      | XRD, SEM, and UV-vis        | [130]|
| AgNO₃/PVP                      | EG            | FeCl₃         | 5 hr 130°C                        | NW                      | TEM                         | [110]|
| AgNO₃/PVP                      | EG            | TBADCB        | 30 min at 120°C                   | NW                      | SEM, XRD, and SPS           | [131]|
| AgNO₃/PVP                      | EG            | NaCl, FeCl₃, Fe(NO₃)₃, and KNO₃ | 2.5 hr 150°C | NW                      | XRD, SEM, TEM, and UV-vis   | [132]|
| AgNO₃/PVP (in presence of dilute HCl) | EG            | —             | 170-190°C                        | NW, NC, and NP          | TEM and UV-vis              | [95]|
| AgNO₃/PVP                      | EG            | NaCl, KBr     | 1 hr 160°C                        | SEM, TEM, EDS, EDX, XRD, XPS, and UV-vis | [111]|

AgNO₃/NaCl/NaBr:
- 80/2/0
- 80/0/2
- 800/2/1
| Regent precursor/capping agent | Reducing agent | Salt mediator | Reaction time, temperature/heating | Morphology & dimensions | Characterization techniques | Ref. |
|-------------------------------|---------------|---------------|-----------------------------------|------------------------|---------------------------|-----|
| AgNO₃/PVP EG/DG NaCl and KBr | 5 hr 145°C    | NW Diameter: 35 nm Aspect ratio: > 1000 | SEM, TEM, and XRD [134] |           |                           |     |
| AgNO₃/PVP EG CuCl₂ and KCl  | 20-30 min 167°C | NW Aspect ratio: 800 | SEM [112] |           |                           |     |
| AgNO₃/PVP EG NaCl and NaBr  | 60 min 150°C | NW Diameter: 16 nm Aspect ratio up to 3000 | TEM, HRTEM, UV-vis, and XRD [136] |           |                           |     |
| AgNO₃/PVP EG NaCl and NaBr  | 60 min 160°C | NW Diameter: 13 nm Aspect ratio up to 3000 |                          |           |                           |     |
| AgNO₃/PVP EG NaCl and NaBr  | 90 min 160°C | NW Diameter: 20-50 nm Length: 30-60 μm | SEM, TEN, and HRTEM [113] |           |                           |     |
| AgNO₃/PVP EG MnCl₂ and NaBr | 4 hr 120°C | NW Diameter: 20-50 nm Length: 4-7 to 20-34 μm | SEM, TEM, and XRD [114] |           |                           |     |
| AgNO₃/PVP EG FeCl₃          | 8 hr 130°C   | NW Diameter: ~ 55 nm Length: ~ 220 μm | SEM, TEM, and HRTEM [137] |           |                           |     |
| AgNO₃/PVP EG NaCl and Fe(NO₃)₃ | 15 hr 110°C | NW Diameter: 45 nm Length: 40 μm | SEM, TEM, HRTEM, XRD, and UV-vis [140] |           |                           |     |
utilized a novel segmented flow reactor consisting of a binary pump module, a reactor heater, and a 10 mL perfluoralkoxy (PFA) reaction coil tubing to synthesize AgNW at 130 °C with lengths up to 36.4 μm and diameters as small as 95 nm by controlling PVP MW. They showed that a higher PVP MW corresponding to longer PVP chain length led to a longer length and smaller diameter of the synthesized AgNWs [145].

Hemmati et al. in another study addressed the challenges in the polyol batch synthesis of AgNW such as low yield and low aspect ratio of AgNWs, presence of other nanostructures as byproducts, irregular morphology of the wires, and long reaction time. They introduced a millifluidic polyol synthesis of AgNWs at lower temperature compared to the batch process. They were able to achieve near 100% yield of high aspect ratio AgNWs in a continuous manner [146, 147].

From this overview of recent studies on the polyol synthesis of AgNWs, it is clear that the obstacles and challenges to control the morphology with a high aspect ratio have been overcome through methods such as introduction of a salt mediator, control of the injection rate of AgNO₃, optimization of sonication time for AgNO₃ solution preparation, control of stirring power, addition of DIW as a solvent or cosolvent, and application of millifluidic or flow reactors.

Figure 1 shows a timeline in which dark gray indicates a method that is well studied and light gray indicates processes in the early stage of their development, where work in the near future is likely to be centered. The corresponding starting year for each method is shown as well.

4. Reaction Mechanism of AgNW Polyol Synthesis

An understanding of the reaction mechanism and dynamics in the polyol synthesis of AgNW allows reaction optimization in terms of conditions such as temperature and reagent concentrations. To reach this goal, it is essential to know how different factors in the synthesis affect wire morphology, for instance, what is the mechanism to facilitate the growth of initially formed seeds to the wire shape by the anion and cation provided from a salt mediator and what are the kinetics behind the application of polymeric reagents as a capping agent, a stabilizer, or a growth director? Finally, the steps governing formation of AgNWs must be clarified.

Several studies used methods such as microscopic and spectroscopic characterizations (TEM, HRTEM, SEM, UV-vis, …) to assess the reaction mechanism. Schuette et al. utilized AgCl nanocubes of various sizes as heterogeneous nucleants to synthesize AgNW through the polyol process. As the AgNW diameter was almost independent of AgCl size, they showed that the nucleation event had little influence on AgNW diameter. Their kinetic investigation showed that AgNW length, diameter, and aspect ratio grow in parallel. Consequently, they showed that growth is limited by the rate of reduction through a surface-catalyzed reduction at which Ostwald ripening or aggregation of NPs are essential components of the growth mechanism [105]. Mao et al. used a self-seeding process and proposed a reaction mechanism based on the adsorption of PVP onto the {100} surface of the silver seeds confining growth to the {111} surface [58]. Lai et al. produced Ag/Ag homojunction NWs (HNWs) by an effective and simple solvothermal method and showed that the Ag/Ag HNW synthesis is sensitive to PVP concentration and reaction temperature [89]. Liu et al. utilized a (NH₄)₂CO₃-mediated polyol process instead of a conventional salt-mediated process for improvement of AgNW purity and showed that the synthesized AgNWs have rounded instead of faceted ends on the {111} crystal plane. They proposed that in the presence of PVP and (NH₄)₂CO₃, the initial multiple twinned particles (MTPs) with twin boundaries grow into AgNWs with rounded ends instead of faceted ends on the {111} crystal plane. They explained that the seeds are produced by the reduction of Ag ions in boiling water, with sodium hydroxide and sodium citrate as additives, and subsequently AgNWs are
produced. They performed molecular dynamic computations with an embedded atom method to compare with the experimental results [148]. Wu et al. developed a growth model based on their observation of coarsening and combination of Ag nanorods by syringe rate testing [93]. Whitcomb et al. evaluated the growth mechanism in a high-temperature polyl process through both potentiometric Ag ion measurements and incorporation of nitric oxide monitoring to clarify the crystal growth process during the reduction of Ag ions to metallic Ag. They concluded that the reduction of Ag ions and growth of AgNWs include a series of discrete phases, from AgCl precipitation to Ostwald ripening [149]. Wang et al. investigated the seeding protocol for high-concentration synthesis of AgNWs. Based on AgNW nucleation and growth behavior, they found a linear relation between nucleation and the Ag + and Cl − concentrations. Based on the proposed mechanism, they reported synthesis of high quality of AgNWs at which Ag + concentrations are twenty times higher than the previously reported polyl process. They also demonstrated control of AgNW diameter through the size of the AgCl seeds [150]. Abbasi et al. tried cobalt chloride (CoCl2) as a salt mediator or a growth-promoting additive in the presence of an optimum ratio of glycerol/water (G/W) as solvent to synthesize AgNW not only in a rapid way but with ability to control the AgNW morphology as well. They also proposed a growth mechanism based on the AgCl formation monitoring, an important intermediate stage in generation of AgNWs [109]. Li et al. described a hydrothermal reaction mechanism similar to the polyl process in which pentagonal twinned silver seed crystals with D5h symmetry are produced and subsequently increase in diameter. The reaction requires a stationary solution and a relatively high temperature with high molecular weight PVP to produce long AgNWs [130]. Jang et al. proposed a four-step reaction mechanism including nucleation, cluster formation, seeding, and AgNW growth with assistance of PVP [131]. Wei et al. explained the reaction mechanism behind the formation of segmented AgNWs including the initial steps of formation of single nanowires with assistance of a salt mediator and a capping agent. They attributed the formation of segmented wires to the higher potential energy of the end atoms causing them to diffuse to the sides or attach end to end to reduce the surface chemical potential [132]. Tang et al. described a detailed reaction mechanism in the polyl process involving an etching effect. In this mechanism, the ligand concentration is higher in the nucleation step and lower in the growth step and maximizes the benefit of etching in the latter. The mechanism entails a transition from ligand-rich aggregates of PVP to an uneven ligand distribution with PVP deficiency. The reason is that the silver ions coordinate better with repeating units of PVP as a capping agent. With more silver ions released as the reaction continues, the restricting motion of PVP will limit its coordination with silver ions, which promotes etching [133]. Rui et al. introduced the application of electron trap distribution (ETD) to explain the growth mechanism of wires with different diameters and yields. They showed that by simultaneous application of NaCl and NaBr as salt mediators, AgBr1-xClx would be formed as a mixed silver halide crystal with uniform EDT which is beneficial for the formation of high aspect ratio AgNWs. The x value, defined as \( x = [\text{NaCl}]/([\text{NaCl} + \text{[NaBr]}]) \), controls the diameter and yield of AgNWs [111].

Hemmati et al. also showed that the growth mechanism includes three steps of reduction, nucleation, and growth, and by SEM characterization of nanostructures obtained at different stages of the reaction (every 15 minutes) as shown in Figure 2. This mechanism illustrates that the small silver nanoparticles start to dissolve, as they are not stable in the solution. In the presence of PVP acting as a capping agent that selectively adsorbs on {100} facets of the silver nanocrystals, 1D silver nanostructures begin to grow. The chloride ions provided by CuCl2 form AgCl reducing the concentration of silver ions and releasing them slowly at the beginning of the reaction. The Cu2+ is reduced to Cu+ by EG and assists the growth of AgNWs by scavenging oxygen atoms from the surface of the silver seeds. Purging with Argon gas during the reaction also acts to remove oxygen. In summary, silver ion reduction, nucleation in the presence of salt mediator, and wire growth with assistance of PVP acting as a capping agent are the three main steps in the synthesis of AgNWs through the polyl synthesis process [9, 147]. A schematic illustration of the AgNW polyl reaction mechanisms and kinetics according to various studies is shown in Figures 3–6. All of these results regarding the polyl AgNW synthesis emphasize the necessity to precisely control reaction parameters such as temperature, salt mediator type and concentration, capping agent MW, and concentration to synthesize high-quality, high-aspect ratio AgNW with high yield.

5. Lessons from Polyl AgNW Synthesis toward Green and Sustainable AgNW Synthesis

Green noble nanoparticle syntheses utilizing natural precursors are of great interest because of cost effectiveness, facile reactions, less harmful feedstocks and procedures, and sustainability. These green technologies can be achieved by the application of green reagents including the reducing agent, solvent, and capping agent. Due to the need for environmentally friendly technologies for nanomaterial synthesis, a synergy between biotechnology and nanotechnology has led to consideration of biosynthesis of nanostructures. Taking advantage of biological materials in nanoparticle synthesis is one of the most promising approaches in modern nanoscience because the formation of nanostructures by organisms is a highly evolved and broad family of processes. Nowadays, green noble nanoparticle synthesis processes utilizing natural precursors are of great interest because they are cost effective, facile, benign, and sustainable. However, these new techniques should be optimized not only in terms of scale-up capability but also in product quality and performance. Although there are many published studies regarding the chemical synthesis of 1D metal nanostructures, there are comparatively few regarding green methods. For instance, Lin et al. used broth of Cassia fistula leaf as a reducing and capping agent to synthesize AgNWs with diameter of 50–60 nm and length up to tens of micrometers. Based on the FTIR characterization, they found that some water-
soluble polyhydroxy components, such as alkaloids, flavonoids, and polysaccharose, were acting as capping ligands in AgNW formation. Based on the TEM images of the synthesized particles during the reaction, they found that the growth of AgNWs is due to the recrystallization of nanoparticles next to each other in a linear fashion rather than point-initiated growth of initially formed seeds [151]. Ma et al. utilized glucose to synthesize AgNWs for silver nanowire-silver nanoparticle-graphene nanosheet composite fabrication [152]. Jeevika et al. used clove oil (Syzygium aromaticum) that contains 81-95% phenols as a green reducing agent to synthesize AgNW in the diameter range of 30-80 nm with lengths of 2–5 μm at room temperature. They also showed that the size and morphology of the synthesized nanostructures are sensitive to AgNO₃ concentration [153]. In another study, Nadagouda et al. demonstrated synthesis of various morphologies of silver and palladium nanostructures including nanorods and nanowires using vitamin B₂ acting as both a reducing agent and a capping agent in various solvents such as water, isopropanol, acetone, and acetonitrile. They showed that the morphology and size of the resulting nanostructures depend on the solvent used for the preparation. For instance, nanorods are produced in water whereas thick nanowires are produced in isopropanol [154]. Wang et al. formed dendritic silver nanostructures (DSNs) using ascorbic acid as a reducing agent and clove oil as a capping agent under an ultrasound [155]. Flores-Gonzalez et al. used two different green teas: Mexican tea (Royal Tea, Mexico) and Korean tea (Boseong green tea), containing Camellia sinensis as a reducing agent in the presence of PVP at low concentration and MW of 40,000 to synthesize AgNW with diameter around 50 nm and length of...
1.3 μm. They attributed the reduction ability of this green reducing agent due to the presence of epigallocatechin, epicatechin, epicatechin-3-gallate, and epigallocatechin-3-gallate (EGCG) [156]. Feiz Soleimani et al. synthesized different morphologies of silver nanostructures such as nanocubes, nanospheres, nanorices, and nanorods with blunt and sharp ends using medium molecular weight starch, glucose, and chitosan in acetic acid solution at different reaction conditions. They found that both chitosan and starch can selectively adsorb on {100} facets of initially formed silver seeds and facilitate the growth of AgNWs in the {111} direction as PVP does in the polyol process as a capping agent [157].

Recently, Dong synthesized single-crystal silver nanowires with lengths up to tens of micron and diameters of 50 nm utilizing tannin, a naturally occurring plant polyphenol, functioning as both reducing and stabilizing agents at temperatures of 45–55°C. They reported that a slow reaction rate favors anisotropic growth of nanowires and the reducing ability of tannin is due to oxidization of its hydroxyl groups. By FTIR characterization, they found that there is a remarkable change in the hydroxyl group during synthesis. Tannin exhibits a broad peak in the region of 3300–3500 cm⁻¹ corresponding to –OH groups. However, extremely weakened peaks were observed after AgNW synthesis, which shows the involvement of hydroxyl groups in the formation of the Ag nanowires [158]. Hemmati et al. recently showed that Maui Raw Turbinado brown sugar acts simultaneously as a reducing and capping agent in synthesis of 1D silver nanostructures at low temperature (25-50°C) [159].

6. Concluding Remarks and Future Directions

Based on the review of studies of polyol synthesis of AgNWs, there have been much investigation and substantial progress in batch synthesis of AgNWs by the polyol process. Most of these synthesis methods are carried out on small scales and are designed for optimization, parametric study, or
mechanistic investigation of the reaction mechanism. The challenges in batch synthesis of AgNWs on large scales include difficult reaction control resulting in batch to batch variations and production of morphologies other than AgNWs resulting in low yield. Synthesis of AgNWs is normally time consuming and the final cost of available commercial products is high. The polyl flow synthesis in the millifluidic reactor overcomes these challenges through mixing control in small volumes in a continuous manner. Continuous polyl synthesis of AgNWs is scalable and can produce a high yield of AgNWs in large volume continuously. Moreover, the green chemistry synthesis of nanoparticles has recently gained much attention raising the possibility of alternative energy efficient, safe, and environmentally benign paths to nanomaterial synthesis. Nowadays, the need for sustainable development regarding the environment has stimulated research on green synthesis [12]. As a result, a synergy between biotechnology and nanotechnology as biosynthesis of nanostructures is inevitable and taking advantage of biological materials in nanoparticle synthesis is one of the most promising approaches in modern nanoscience [13, 160]. Therefore, the strategy of utilizing the reducing capabilities of green reducing agents directly in nanomaterial synthesis known as green chemistry synthesis of nanomaterials has great advantages in 1D metal nanostructure synthesis [161]. There are a few studies regarding small-scale green synthesis of AgNWs utilizing various green reducing agents and capping agents such as clove oil and vitamin B2 [153, 154].

Future research in the area of polyl synthesis of AgNWs is expected to emphasize large-scale polyl millifluidic synthesis of AgNWs in large volume continuously and in high yield to dramatically reduce cost. In addition, a primary goal will be to take advantage of green and millifluidic synthesis to develop a millifluidic green synthesis of AgNWs using water as solvent for biodegradability and low toxicity. Chemical nanoparticle synthesis from metal salts in most current processes involves harsh chemicals, surfactants, and additives. On the other hand, green synthesis is aimed at applying natural extracts as a reducing agent with inherent growth termination, stabilization, and capping characteristics [162–164]. However, these new techniques should be optimized not only in terms of scale-up but also with respect to product quality and performance. Moreover, future research is expected to focus on optimization of the both polyl millifluidic and green millifluidic synthesis of AgNWs with respect to the millifluidic reactor parameters such as residence time, temperature, and reagent injection rates. The objective is a large scale, smart, green, inexpensive, environmentally friendly, and continuous process for AgNW synthesis on the foundation of the chemical synthesis methods reviewed in this study. Finally, in situ X-ray adsorption spectroscopy (XAS) is a versatile technique that provides an opportunity to investigate the reaction dynamic and mechanism of AgNW growth in a millifluidic reactor to further control their morphology, size distribution, and crystal structures. In future research, both in situ XAS characterization and millifluidic reactor design hold promise for probing the reaction mechanisms and dynamics of nanostructure synthesis at the atomic level [165].

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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