Parameters of Silver Nanowire Synthesis by Polyol Method

Qianrui Wang *

Department of Chemistry and Chemistry & Biochemistry, Rose-Hulman Institute of Technology, Terre Haute, Indiana 47803, U.S.A.

* Corresponding Author Email: wangq5@rose-hulman.edu

Abstract. With an innovative combination of high electrical conductivity, optical transparency, and mechanical flexibility that outperforms conventional material like indium tin oxide (ITO), silver nanowires (AgNWs) have become the leading option for next-generation transparent conductors in devices such as flexible displays, OLEDs, and solar cells.. This review offers a comprehensive overview of the polyol process, the dominant and most widely used technique for synthesizing AgNWs. Despite the advantages, achieving high-quality AgNWs remains a challenge, necessitating precise control over numerous variables. Discussed the critical roles of chemical reagents in controlling the nucleation and anisotropic growth of the nanowires in details, including roles of silver source, the poly(vinyl pyrrolidone) (PVP) as a facet-selective capping agent, and various mediating halide salts. The review also give a detailed account of the impact of physical process parameters, including reaction temperature, time, and stirring rate, on the reaction kinetics and final morphology of the produced product. Achieving high-quality AgNWs requires a delicate balance of these chemical and physical factors to achieve the desired aspect ratio and yield for advanced applications.

Keywords: Silver nanowires; polyol synthesis; transparent conductors; transparent electrodes.

1. Introduction

One-dimensional (1D) metallic nanostructures like silver nanowires (AgNWs), have earned interest from scientific and industrial studies, due to their unique properties, which are better than their bulk counterparts [1,2]. Their exceptional characteristics have made them a leading candidate for next-generation material, especially in transparent conductors (TCs). Decades before AgNWs, indium tin oxide (ITO) had dominated the transparent conductors market, such as touch screens, photochromic color-changing glasses, flat-panel displays, and solar cells. However, ITO has significant drawbacks. ITO is a brittle ceramic, which limits the sputtering process and makes its deposition slow and costly.

Additionally, the scarcity of indium presents long-term supply and cost issues [3]. These limitations make researchers search for a better, higher-performance, solution-coatable alternative. Among the various candidates, including conducting polymers, carbon nanotubes, and graphene, metal nanowire networks have demonstrated the ability to meet and even exceed the applications that previously required ITO [2].

AgNWs have become a powerful competitor within new generation materials because it is a unique combination of three better properties: electrical conductivity, optical transmittance, and mechanical flexibility [3]. Among all metals, bulk silver conducts electricity and heat the best, and this property is retained at the nanoscale. When a sparse layer of these highly conductive AgNWs is coated onto a substrate (such as glass), it forms a network that is electrically conductive and remains transparent, as nanoscale structures allowing light to pass through the voids between the wires.

Moreover, silver nanowire films are inherently flexible. This made them prominent as transparent electrodes in flexible touch screens, organic light-emitting diodes (OLEDs), thin-film solar cells, and other wearable devices, competing with ITO ceramics and in many cases outperforming it [3,4].

Beyond transparent and flexible conductors, the high surface area and unique electronic properties make AgNWs suitable for advanced sensors. Additionally, the potential of using silver nanowires as catalysts has been explored for various reactions. As research progresses, AgNWs are also being investigated and tested for in-body biomedical applications, as the conductivity is suitable for implantable sensors and other similar electronic devices.

Various techniques have been reported and tested to create one-dimensional silver nanowires. These techniques, include physical methods, like evaporation-condensation and arc discharge methods, as well as chemical approaches using solution-phase chemical synthesis to find the best combinations of reaction parameters to provide the best control, yield, and scalability. Among these methods, the polyol process is the most prominent and widely used method for producing high-quality silver nanowires for commercial applications and research uses. Following sections will discuss the synthesis of silver nanowires in depth.

2. Synthesis of silver nanowires

2.1. Challenges in silver nanowire synthesis

Despite the promising potential of silver nanowire products, the adoption of silver nanowires is still facing persistent challenges in their synthesis and processing [5]. One primary issue is achieving uniformity in the dimensions of the nanowires: the aspect ratio (length-to-diameter ratio) of the constituent nanowires will significantly affect the performance of a transparent conductive film. Therefore, it is critical to achieve a consistent and controllable diameter and length when producing AgNWs for reliable, high-performance devices.

Another major challenge in silver nanowire production is how to improve synthesis efficiency. To become a truly cost-effective alternative for ITO, silver nanowire production must be scalable, rapid, economical, and environmentally friendly. As a result, developing a synthetic route that maximizes the yield, shortens the reaction time, and minimizes the cost of reagents and energy is crucial. Many current methods, however, are time-consuming and may not be easily scalable.

Purification of the product is also an aspect that researchers need to keep modifying. The polyol process of silver nanowire production is the most important and widely used wet-chemical synthesis method. However, polymer method synthesis will inevitably produce zero-dimensional (0D) silver nanoparticles (AgNPs) as a byproduct, which will negatively affect the performance of transparent conductive films, because they will increase light scattering [6]. Furthermore, it is often difficult to separate the nanoparticles from the desired silver nanowire products with traditional methods, like centrifugation or vacuum filtration [7]. It is non-debatable that developing a simple, scalable, and effective purification method by utilizing existing techniques, such as the selective precipitation [6], is important for reaching the highest possible performance from silver nanowire products.

2.2. Not commonly used synthesis methods

Polyol process is the dominant and most straightforward technique to synthesize metal nanostructures in small batches, but other methods have been developed, though they might be less common for silver nanowire production.

2.2.1. Template method

Template method is an approach that utilizes a pre-existing structure with nanoscale channels or pores to guide the growth of nanowires. There are “hard” templates, such as porous alumina or polycarbonate membranes, and there are also “soft” templates made from self-assembled structures, like rod-shaped micelles or liquid crystalline phases. Channels on these templates will allow metal deposition within, typically via electrochemical motivation or simple chemical reductions. Template process provides excellent control over diameter; however, it is difficult to scale up and requires a subsequent step to remove the template, which could be hard to do and will damage the nanowires [8,9]. Also, the cost of templates or methods to make the template might not be economical for large-scale production.

2.2.2. Hydrothermal/solvothermal methods

Hydrothermal/solvothermal methods are processes involving chemical reductions in an aqueous solution, which is called hydrothermal, or an organic solution, which is solvothermal, within a sealed

vessel (an autoclave) at elevated temperatures and pressures. The high temperature and pressure can alter the solubility and reactivity of silver sources, such as silver salt, allowing the formation of unique nanostructures. These methods have been used in silver nanowire production, but they're often slower than the polyol process, require a specialized high-pressure source and chamber, and would cost more in terms of energy efficiency.

2.2.3. Microwave-assisted synthesis

Microwave-assisted synthesis utilizes microwave irradiation as the energy source to rapidly heat the reaction solution. Microwave-assisted heating is volumetric and can be specially designed or programmed to be highly efficient and can shorten reaction times from hours to minutes. It has been applied to various solution-phase syntheses as well, including the polyol process to accelerate the formation of silver nanowires and other nanostructures.

2.3. The polyol method

The polyol method is a versatile technique for producing metallic colloids [10]. It was first introduced by Fievet and his group [7] and later adapted for anisotropic nanostructures synthesis by Yugang Sun and co-workers [10]. In a typical process to synthesize metal nanomaterials, silver source (silver salt), capping agent, and mediating agents are dissolved in a high-boiling-point alcohol, or "polyol." This alcohol will work as solvent of the system and a reducing agent, and ethylene glycol (EG) is the most commonly used polyol in the synthesis of silver nanowires.

At elevated temperatures, which are typically between 130-170 °C, EG not only serves as the solvent but also acts as the reducing agent. At this temperature, EG is oxidized to glycolaldehyde, which in turn reduces the silver ions (Ag^+) in silver salts to silver atoms (Ag^0) [10]. Other polyols, such as glycerol, have also been used and possibly offer advantages in some particular systems. It is also noticeable that silver nitrate ($AgNO_3$) is one of the most common sources of silver ions, due to its high solubility in EG and low cost.

Capping agent is a polymer; in most cases, poly (vinyl pyrrolidone) or PVP is used. It is also a structure-directing agent, whose precise mechanism of silver growth is complex, but generally, PVP selectively adsorbs onto the different crystal faces of nascent silver nanocrystals. This selective adsorption passivates the {100} side facets, forcing the growth to occur primarily on the {111} end facets, which leads to desired 1D, anisotropic elongation into a wire-like structure [1, 10]. Besides this, PVP is also a source of steric stabilization, which can prevent nanowires from aggregating in the solution.

Also, a small quantity of metal halide salt is introduced to the system under control. These are mediating agents, which essentially promote the growth of nanowires. Mediating agents are optional, but it is critical if high-yield and high-aspect-ratio nanowires are required. The halide anions, (e.g., Cl^- or Br^-) react with Ag^+ to form less soluble silver halide nanoparticles, such as AgCl , which act as heterogeneous nucleation sites and control the concentration of the free silver ion in the solution. This prevents the explosive nucleation that would lead to a high yield of 0D silver nanoparticles. The metal cations, such as Cu^{2+} and Fe^{3+}, will act as an oxidative etchant, combining oxygen, remove defective seed, and prevent the oxidative dissolution of the desired nanowire seeds required for wire growth [1,11].

The whole synthesis route begins by reducing silver ions (Ag^+) to form silver atoms, which then aggregate into multiply twinned particles (MTPs), which typically have a decahedral shape. With the presence of poly (vinyl pyrrolidone) polymer capping agents and metal halide mediating agent, these MTPs serve as seeds that grow anisotropically into long, thin nanowires [3].

3. Influence of reagents during synthesis process

To produce high-quality silver nanowires by utilizing polyol synthesis, the reaction is critically dependent on a delicate balance of concentrations of reagents described in section 2.1. The reactions between the silver source, the capping agent, and various mediating salts control the reaction kinetics,

nucleation speed, and growth rate directly, affecting the final morphology, aspect ratio, and purity of the silver nanowire product. A thorough understanding of the role of each reagent is essential to find the balance between their concentrations.

3.1. Mediating agents

The addition of a controlled amount of metal halide salt is essential to high-yield polyol synthesis. Halide salts provide both cations and anions that affect reactions distinctively but synergistically.

3.1.1. Halide anions

Most seen halide ions from mediating agents in polyol synthesis of silver nanowires are chloride (Cl^-) and bromide (Br^-), which are crucial for controlling the nucleation phase of the reaction. In their absence, the rapid reduction of silver ions (Ag^+) leads to supersaturation and explosive homogeneous nucleation and will result in a high yield of 0D nanoparticles [12]. When these halide anions are introduced, however, they react with silver ions to form some silver halides, which are less soluble AgCl (or AgBr) [11], and they serve as heterogeneous nucleation sites for the growth of silver. Also, silver halides will be creating a buffer solution environment that slowly releases free silver ions back to the reaction system. The slow release of Ag^+ effectively mimics the controlled and slow addition of silver ions via a syringe pump or titration equipment, which can prevent supersaturation and favor the thermodynamically stable MTP formations, which are required for anisotropic wire growth [13, 14].

Besides, the choice of halide anion and the selection of their concentration are also critical. Chloride ions are widely available and commonly used because they have an etching effect on silver seeds, which selectively dissolve single-crystal seeds and have more stable MTPs left behind. However, it has been confirmed that an excessively high concentration of chloride ions can lead to the oxidative etching of MTPs, reducing the overall yield of silver nanowires.

Bromide ions have been seen to be particularly effective in controlling the diameter of the nanowires. An author demonstrated this conclusion by systematically increasing the concentration of NaBr in the synthesis. Furthermore, the reported diameter of the resulting silver nanowires was reduced from 72 nm to 20 nm [6]. This effect was considered to be caused by an increase in the number of AgBr nucleation sites, which allows the formation of a greater number of thinner nanowires for a given amount of silver source.

3.1.2. Metal cations

Most common metal cations seen in mediating agents are copper (Cu^{2+}), iron (Fe^{3+}), and sodium ions (Na^+). They are important for protecting the nascent seeds and promoting the growth of the wire. In an aerobic environment, ethylene glycol will dissolve some amount of oxygen (from the air), which can adsorb onto the surface of silver seeds and cause oxidative etching, which dissolves the seed and inhibits wire growth. Cations, like Cu^{2+} and Fe^{3+} acts as a catalyst in a redox cycle to scavenge this adsorbed oxygen. In a typical process, Cu^{2+} is reduced by ethylene glycol to Cu^+ which then reacts with adsorbed atomic oxygen and removes them from the silver seed surface and is re-oxidized to Cu^{2+} in the process [1]. Oxygen is effectively and continuously removed from the solution system in this cycle, and MTPs are protected from oxidative etching. Very long silver nanowires can be made by this mechanism, as reported.

Simple alkali metal ions, Na^+ for example, are also believed to be able to scavenge oxygen but might do so less effectively compared to transition metal ions [1].

3.2. Silver nitrate concentration

As the source of silver ions in the system, the concentration of silver nitrate ($AgNO_3$) impacts the reaction rate and the final morphology of the nanostructures directly. There is a trade-off between reaction yield and the aspect ratio of the product.

At low concentrations of silver nitrate, the reaction is observed to be slower. The slower reduction from ion to silver atoms favors the formation of fewer nucleation sites, allowing the silver atoms to

contribute to the growth of existing seeds. This condition typically results in the formation of nanowires with smaller diameters, resulting in a higher aspect ratio. However, the overall yield of silver nanowires is lower [4].

Conversely, at higher concentrations of $AgNO_3$, reaction will happen at a faster rate of reduction and a higher degree of supersaturation, which promotes a faster nucleation rate. This provides more silver for wire growth and can increase the overall mass yield of silver nanowire crude products; it also significantly increases the formation of nanoparticles [4].

3.3. Poly(vinyl pyrrolidone)

Poly (vinyl pyrrolidone), or PVP, is arguably the most essential reagent for directing the growth of silver nanostructures in the polyol synthesis process. PVP polymer acting as a capping agent and stabilizer.

PVP selectively adsorbs onto the facets of the nascent silver nanocrystals, and it allows a strong affinity for silver surfaces because of the oxygen atom in carbonyl groups in the pyrrolidone rings. It is widely accepted that PVP binds more strongly to the {100} facets than to the {111} facets of silver. As a result, this preferential adsorption is called "capping," which passivates the side surfaces of the MTP seeds, and kinetically hinders their growth in the lateral directions [15]. As a result, the addition of newly formed silver atoms is directed to the less protected {111} end facets, maintaining a one-dimensional growth and resulting in a wire morphology [13]. However, it has also been clarified that, while PVP is essential for preserving the facets and providing steric stabilization to prevent aggregation, it does not inherently promote the formation of one specific facet type over another. In comparison, it stabilizes the facets that are thermodynamically or kinetically favored under the given reaction conditions.

3.3.1. PVP molecular weight

The molecular weight (MW), or the chain length, or the poly (vinyl pyrrolidone), has a significant impact on the outcome of the synthesis. It has been demonstrated that as the MW of PVP increases the yield and aspect ratio of the silver nanowires dramatically improved. Longer chain PVP is more effective at wrapping around the silver seeds and providing robust steric protection. It has been proposed that the longer polymer chains can coordinate more silver ions, arranging them in a linear fashion that promotes the formation of 1D silver embryos, which will grow into nanowires. In contrast, using a very low MW polymer of PVP often results in a higher proportion of nanoparticles, as the shorter chains are less effective at directing anisotropic growth.

3.3.2. Molar ratio of poly(vinyl pyrrolidone) to AgNO3.

The ratio of poly (vinyl pyrrolidone) repeating units to silver ions is another critical parameter that could affect the reaction. At a low ratio, there is insufficient PVP to effectively guide and cap all the crystal facets of the growing seeds, which leads to more isotropic growth, producing thicker nanowires in diameter or a higher yield of nanoparticles [12]. Conversely, if the ratio is too high, excess PVP can overly inhibit growth by capping all facets, preventing the desired {111} growth facets, reducing the overall yield and length of the silver nanowires [13].

4. Process parameters in polyol synthesis

Beyond the chemical composition of the reaction mixture, reaction temperatures, time, and stirring rate are also reported to play a crucial role in dictating the kinetics of nucleation and growth. These parameters are interconnected and must be carefully controlled at the same time to achieve reproducible, high quality synthesis of silver nanowires.

4.1. Reaction temperature

Reaction temperature is one of the most critical parameters in the polyol process, as it directly controls the reduction rate of silver nitrate by ethylene glycol. The conversion of EG to its more

reductive aldehyde form, glycolaldehyde, is temperature dependent so that it only becomes significant and faster at temperatures above 140°C [16]. The choice of temperature creates a delicate balance between nucleation and growth kinetics.

At low temperatures (e.g., 100-13°0C), the reduction of Ag^+ is slow. This slow reaction rate favors a growth-dominant system, where only a few nuclei that form could have time to grow into longer nanowires. The low temperature may not provide sufficient thermal energy input to fully reduce the silver ions, which will cause a low overall yield and incomplete reactions.

At elevated temperatures (e.g., 160-180°C), the reduction of Ag^+ by EG is significantly accelerated. This leads to a rapid increase in the concentration of silver atoms, causing the nucleation rate to become very fast, and the result is the formation of a large number of multiply-twinned seeds. But high temperatures will also dramatically increase the likelihood of producing undesirable nanoparticle byproducts. If the temperature is too high, exceeding 185°C, the adsorption of PVP onto the silver surface weakened, causing more isotropic growth and the formation of nanorods, or could make spherical particles instead of long nanowires [9].

Therefore, for the polyol process of silver nanowire synthesis, an optimal temperature is required. Within this range, the reduction rate is fast enough to ensure a high yield but controlled enough to favor the anisotropic growth of nanowires over the explosive nucleation of nanoparticles.

4.2. Reaction time

The duration of the reaction is another key parameter that could influence the final morphology and purity of the silver nanowire product. The growth of the nanowire product is controlled by a complex kinetic process, most notably Ostwald ripening.

Initially, the rapid reduction of silver ions leads to the formation of a mixture of small silver nanoparticles and multiply-twinned seeds [16,17]. As the reaction goes forward, Ostwald ripening becomes the dominant mechanism. In this process, less stable and smaller manoparitcles have a higher surface energy, so they tend to dissolve back into the reaction system or the solution. The dissolved silver atoms then redeposit onto the surface of the larger, more thermodynamically stable structures, such as growing nanowires [16]. This leads to a gradual increase in the average length and diameter of the nanowires over time, while the number of nanoparticle byproducts decreases. For example, it has been reported that nanoparticles formed within the first ten minutes of the reaction were then developed into nanowires that continued to grow for up to 120 minutes [17].

However, extended reaction time is not always beneficial. Noted that after an initial growth phase, extended reaction times could lead to the etching of the nanowires, causing their surfaces to become rough and decreased diameters.

4.3. Stirring rate

The stirring or agitation rate of the reaction mixture has an effect on the synthesis outcome as well. Adequate stirring is essential to ensure the homogeneous mixing of reactants and to maintain a uniform temperature throughout the solution [9]. This uniformity is crucial for achieving a controlled and reproducible synthesis.

Another effect is that stirring also introduces oxygen from the atmosphere into the reaction solution. Oxygen can act as an oxidative etchant, as discussed previously, and needs to be carefully controlled, as oxygen can help to dissolve unstable single-crystal seeds, and also can lead to oxidative etching of the growing nanowires if there is excessive oxygen present [9]. Furthermore, vigorous stirring can physically disrupt the growth of long nanowires or even cause them to break.

5. Conclusion

Silver nanowires are a promising material in the field of material science and chemical technology. Their unique combination of high electrical conductivity, optical transparency, and mechanical

flexibility makes them an ideal replacement for the brittle and expensive ITO that currently dominates the industry and market.

This review provided a comprehensive overview of the synthesis of silver nanowires by the polyol method, which is widely adopted. The successful synthesis of high-quality silver nanowires is a complex multiparameter problem that requires a full understanding of the relationship between chemical reagents and physical process conditions. Every chemical reagent is critical in controlling the nucleation and anisotropic growth of the nanowires. Furthermore, process parameters such as reaction temperature, time, and stirring rate must be carefully balanced and optimized to provide ideal reaction kinetics and achieve the desired morphology and aspect ratio.

References

[1] Johan, M. R., Aznan, N. A. K., Yee, S. T., et al. Synthesis and Growth Mechanism of Silver Nanowires through Different Mediated Agents (CuCl2 and NaCl) Polyol Process. Journal of Nanomaterials, 2014, 2014(1): 105454.

[2] Ha, H., Amicucci, C., Matteini, P., et al. Mini review of synthesis strategies of silver nanowires and their applications. Colloid and Interface Science Communications, 2022, 50: 100663.

[3] Ye, S., Rathmell, A. R., Chen, Z., et al. Metal Nanowire Networks: The Next Generation of Transparent Conductors. Advanced Materials, 2014, 26(39): 6670–6687.

[4] Lin, J.-Y., Hsueh, Y.-L., Huang, J.-J., et al. Effect of silver nitrate concentration of silver nanowires synthesized using a polyol method and their application as transparent conductive films. Thin Solid Films, 2015, 584: 243–247.

[5] Yang, L., Huang, X., Wu, H., et al. Silver Nanowires: From Synthesis, Growth Mechanism, Device Fabrications to Prospective Engineered Applications. Engineered Science, 2023.

[6] Li, B., Ye, S., Stewart, I. E., et al. Synthesis and Purification of Silver Nanowires To Make Conducting Films with a Transmittance of 99%. Nano Letters, 2015, 15(10): 6722–6726.

[7] Fievet, F., Lagier, J., Blin, B., et al. Homogeneous and heterogeneous nucleations in the polyol process for the preparation of micron and submicron size metal particles. Solid State Ionics, 1989, 32–33: 198–205.

[8] Kaabipour, S. and Hemmati, S. A review on the green and sustainable synthesis of silver nanoparticles and one-dimensional silver nanostructures. Beilstein Journal of Nanotechnology, 2021, 12: 102–136.

[9] Kumar, A., Shaikh, M. O., and Chuang, C.-H. Silver Nanowire Synthesis and Strategies for Fabricating Transparent Conducting Electrodes. Nanomaterials, 2021, 11(3): 693.

[10] Sun, Y., Yin, Y., Mayers, B. T., et al. Uniform Silver Nanowires Synthesis by Reducing AgNO3 with Ethylene Glycol in the Presence of Seeds and Poly(Vinyl Pyrrolidone). Chemistry of Materials, 2002, 14(11): 4736–4745.

[11] Korte, K. E., Skrabalak, S. E., and Xia, Y. Rapid synthesis of silver nanowires through a CuCl- or CuCl2 -mediated polyol process. J. Mater. Chem., 2008, 18(4): 437–441.

[12] Coskun, S., Aksoy, B., and Unalan, H. E. Polyol Synthesis of Silver Nanowires: An Extensive Parametric Study. Crystal Growth & Design, 2011, 11(11): 4963–4969.

[13] Hemmati, S., Harris, M. T., and Barkey, D. P. Polyol Silver Nanowire Synthesis and the Outlook for a Green Process. Journal of Nanomaterials, 2020, 2020: 1–25.

[14] Xiao, N., Chen, Y., Weng, W., et al. Mechanism Understanding for Size Regulation of Silver Nanowires Mediated by Halogen Ions. Nanomaterials, 2022, 12(15): 2681.

[15] Mao, H., Chen, J., He, L., et al. Halide-Salt-Free Synthesis of Silver Nanowires with High Yield and Purity for Transparent Conductive Films. ACS Omega, 2023, 8(8): 7607–7614.

[16] Patil, S., Kate, P. R., Deshpande, J. B., et al. Quantitative understanding of nucleation and growth kinetics of silver nanowires. Chemical Engineering Journal, 2021, 414: 128711.

[17] Septiningrum, F., Roza, L., and Fauzia, V. The effect of temperature and reaction time on the shape of Ag nanowires synthesized using the polyol method. IOP Conference Series: Materials Science and Engineering, 2019, 622(1): 012031.