Syntheses of Silver Nanowires in Liquid Phase

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1. Introduction

Nanowires which were defined as having at least two dimensions between 1 and 100 nm, have received a great interest due to their unique optical, electrical, magnetic, and thermal properties with dimensionality and size confinement [1-10]. The intrinsic properties of nanowires are mainly determined by its size and composition. In order to study the size dependent properties, it is the crucial task to synthesize size-controlled nanowires. Among all these nanowires, the synthesis of silver (Ag) nanowires has been and continues to be an area of active research due to the high electrical and thermal conductivities of bulk silver, which is an important material in many fields. Moreover, silver nanowires have also been used as sacrificial templates to generate other nanostructures such as gold nanotubes, which are difficult to be fabricated [9,10]. The research progress in synthesis strategy is mandated by advancements in all areas of industry and technology. In the past ten years, owing to the efforts from many research groups, splendid strategies were developed for the synthesis of Ag nanowires with various levels of control over the growth parameters.

These synthetics strategies have been conveniently categorized into vapor phase approaches and liquid phase growth approaches. Vapor phase approaches mainly utilize physical methods such as an electronic-beam. Limited by the space of the chapter, we lay a strong emphasis on the introduction of liquid phase synthesis of Ag nanowires. Liquid phase syntheses were most widely used because these approaches have the advantages of nature of homogeneous reaction, wide range of solvents, simple monitoring technology, and low cost. In this article, we review some current research activities that center on Ag nanowires. Representative techniques are discussed and supply a basic understanding of the methods and mechanisms for preparing Ag nanowires.

2. Typical synthetic strategies of Ag nanowires

2.1 Polyol method

Polyol synthesis was originally introduced by Fievet et al. [11] as an excellent method for the synthesis of submicrometer-sized metallic nanoparticles. Xia and co-workers successfully developed this method to the preparation of single-crystal Ag nanoparticles with uniform size and shape using polyvinylpyrrolidone (PVP) as a protecting agent [12]. Now the polyol method has become widely used by many research groups for the synthesis of metal...
nanostructures. Xia et al. synthesized Ag nanowires with higher aspects ratios by injection of ethylene glycol (EG) solutions of AgNO₃ and PVP, added drop-by-drop, at a constant solution temperature of 160 °C [12]. In the polyol process, the introduction of an exotic reagent is considered to be the key factor that leads to the formation of wire-like structures. In their experiments, Ag nanowires are generated using a self-seeding process and EG acts as both solvent and reducing agent. For the formation of silver nanowires, low precursor concentrations and slow addition rates are necessary. By controlling the injection rate, multiple-twinned particles (MTPs) formed at the initial stage of the reduction process could serve as seeds for the subsequent growth of silver nanowires, which is the so-called self-seeding process. At a lower precursor concentration, it is possible to reduce the chemical potential to a relatively low level so as to make MTPs thermodynamically stable because it is bound almost entirely by the lower energy {111} facets [13-15]. At the same time, due to the existence of twin defects at the borders of combined tetrahedron, silver atoms will preferentially deposit on those active sites. Once five-twinned particles have been formed, they will change easily from MTPs to silver nanowires. Figs. 1A-1D show the scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images and XRD of the silver nanowires with a large ratio of length to width. It was found that the morphologies and aspect ratios of Ag nanowires strongly depend on the molar ratio between the repeating unit of PVP and AgNO₃. When the molar ratio between PVP and AgNO₃ was more than 15, the final product was essentially composed of silver nanoparticles. When the molar ratio decreased to 6, the resulted product contained many

Fig. 1. A) SEM and C) TEM images of uniform silver nanowires which were synthesized via the self–seeding polyol process. B) XRD pattern of these nanowires, indicating the fcc structure of silver. D) The TEM image of an individual silver nanowire. The inset gives the microdiffraction pattern recorded by focusing the electron beam on this wire. Reprinted with permission from reference [12f]. Copyright 2002 ACS.
Syntheses of Silver Nanowires in Liquid Phase

27

nanorods. Nanowires were synthesized with the molar ratio of 1.5. If the molar ratio was further decreased to 0.6, nanowires become significantly thicker and some of them were non-uniform along the longitudinal axis. It was generally accepted that for a given coordination reagent such as PVP, it can kinetically control the growth rates of various faces of metal through selective adsorption and desorption on these surfaces. An advantage of this method is that large-scaled synthesis of Ag nanowires is possible. It was believed that the synthetic approach described by Xia et al. [12] can be extended to many other metals by selecting appropriate coordination reagents.

2.2 Salt-mediated polyol method

Based on the PVP-assisted polyol method, Xia and co-workers also developed a salt-mediated polyol process to prepare silver nanowires [12,16]. The addition of a trace amount of salt, such as NaCl, Fe(NO)₃, CuCl₂ and CuCl, has been shown to influence the morphology of the final metal products. Usually salt-mediated synthesis strategy is a simple and effective method which is useful for the mass synthesis of silver nanowires [16]. For example, they synthesized silver nanowires in high yields by reducing AgNO₃ with EG heated to 148 °C in the presence of PVP and a trace amount of NaCl. It was found that oxygen must be removed from the reaction solution in the presence of Cl⁻ anions in order to obtain silver nanowires. Fig. 2 shows the proposed mechanism of oxidative etching and growth of MTPs. Five-twinned decahedral particles were proposed to be seeds of Ag nanowires. The defects among single-crystal tetrahedron subunits of decahedral particles provide high-energy sites for atomic addition, leading to one dimensional Ag products via anisotropic growth along the <110> direction. The addition of chloride causes enhanced oxidation and preferential etching of twinned particles, leaving only single-crystal particles (or seeds) to grow. Under the similar conditions, Xia’s experiment has been carried out under argon which supplied an anoxic condition and the twinned particles that formed in the early stage of the reaction could grow into uniform nanowires [17].

![Fig. 2](https://www.intechopen.com)

Fig. 2. Illustration of the proposed mechanism by which twinned decahedron was etched with the existence of O₂/Cl⁻ and silver nanowire was obtained under argon protection.

In another typical synthesis of silver nanowires by Xia et al. [16a], reduction reaction was carried out through a CuCl or CuCl₂ mediated polyol process but without introducing any inert gases. Both the cation and anion are necessary for the successful production of silver nanowires. It was found that oxidative etching effect was not observed even at a comparably high Cl⁻ concentration. This result was attributed to a decrease in the amount of dissolved O₂ present during the reduction reaction. Fig. 3 shows the role of Cu-containing
salts in the polyol synthesis of Ag nanowires. O$_2$ can adsorb and dissociate on silver surfaces and block the [111] reactive sites from adding Ag atoms efficiently [18,19]. Cu(I) [Cu(II)] can be reduced into Cu(I) by EG] effectively scavenge any adsorbed atomic oxygen from the surface of silver seeds and benefit the growth of silver nanowires. These results suggest that silver nanowires can be achieved more rapidly when oxygen is most effectively removed. A trace amount of Cl$^-$ also acts an important role in the polyol synthesis of silver nanowires. Firstly, it provides electrostatic stabilization for the initially formed silver seeds. Secondly, Cl$^-$ can reduce the concentration of free Ag$^{+}$ ions in the solution through the formation of AgCl nanocrystallites and supply a slow release process of Ag$^{+}$ which facilitates the high-yield formation of the thermodynamically more stable MTPs required for wire growth.

All previous reports of the synthesis of silver nanowires from an AgNO$_3$/Cl$^-$/PVP/EG solution described that it is necessary to remove the oxygen dissolved in the reaction solution in order to achieve the growth of silver nanowires. Recently, our group [20-23] and Gou et al. [24] found that the mechanism described above is not applicable to the synthesis of Ag nanowires under rapid microwave(MW)-polyol method in the presence of Cl$^-$ anions because one dimensional (1D) structures were produced preferentially from unstable decahedrons even in the presence of O$_2$. It was predicted that not only Cl$^-$ from NaCl, but also O$_2$ dissolved in EG probably takes part in the shape-selective evolution of Ag 1D products. We extended the MW-polyol method to an air-assisted method which is carried out in an oil-bath tank. In general, mixtures of nanowires and other spherical and cubic particles are prepared in the polyol synthesis. Therefore, centrifugal separation between nanowires and other products was necessary to obtain nanowires. We have recently prepared Ag nanostructures under bubbling air or N$_2$ gas [25]. Then, we succeeded in the synthesis of monodispersed silver nanowires in high yield (>90% without isolation) under bubbling air through a reagent solution under oil-bath heating from ca. 20 °C to the boiling point of EG (198 °C) for 20 min. Fig. 4 depicts typical TEM images of Ag nanowires obtained under bubbling air and N$_2$. Long nanowires of uniform diameters of ca. 40 nm and lengths of 5–30 μm could be obtained under bubbling air without centrifugal separation of other particles.
Syntheses of Silver Nanowires in Liquid Phase

(Figs. 4A and 4B). On the other hand, mixtures of cubes, bipyramids, and wires were prepared under bubbling N$_2$ (Figs. 4C and 4D). The yield of 1D particles is only 20% because of high yields of cubes and bipyramids under bubbling N$_2$. Similar Ag nanostructures were obtained when we prepared Ag nanostructures without gas bubbling. The yield of nanowires (75%) was an intermediate value between that obtained under bubbling air (90%) and that under bubbling N$_2$ (20%). This result can be attributed to that a small amount of residual O$_2$ gas is dissolved in EG without gas bubbling. It takes part in the production of each Ag nanostructure.

![Fig. 4. Typical TEM images of Ag nanostructures prepared from AgNO$_3$ (46.5 mM)/NaCl (0.3 mM)/PVP (264 mM)/EG mixtures at 198 °C by bubbling of air (A and B) and N$_2$ (C and D). Also shown are crystal structures of 1D products, cubes, and triangular bipyramids.](image)

The growth process of silver nanostructures was also studied by observing ultraviolet-visible (UV-Vis) spectra and TEM images at various temperatures. It is well documented that Ag nanostructures display different SPR bands with different frequencies depending on shapes and sizes, as reviewed by Mock et al. [26] and Wiley et al. [27]. The main SPR peaks for Ag nanorods and nanowires appear at ca. 350 and ca. 380 nm as shown in Fig. 5A at 198 °C. These peaks were attributed to the transversal modes of the 1D products with pentagonal cross sections, corresponding respectively to the out-of-plane quadrupole resonance and out-of plane dipole resonance modes. The SPR bands of cubic (ca. 80 nm edge length) and triangular bipyramidal (75 nm edge length) Ag crystals were observed respectively at 320–800 nm with a peak at ca. 470 and 320–900 nm with a peak at ca. 520 nm [12,26,27]. The peaks described above mutually overlap when mixtures of Ag nanostructures of various shapes and sizes were prepared.
Fig. 5. UV-Vis spectra of Ag nanostructures prepared from AgNO$_3$/NaCl/PVP/EG mixtures under bubbling of (A) air and (C) N$_2$. Also shown are typical TEM images of Ag nanostructures obtained by bubbling of (B) air and (D) N$_2$ at 180 °C.

To examine the shape evolution of Ag nanostructures through bubbling air and N$_2$, the UV-Vis absorption spectra of the reagent solutions were measured at various solution temperatures (Figs. 5A and 5C). UV spectra obtained under bubbling air and N$_2$ are similar at low temperature. A symmetrical SPR band with a peak at ca. 410 nm appears at ca. 100 °C and becomes strong and broad up to ca. 175 °C. This suggests that the formation of spherical nanoseeds and the sizes become large with the increase in temperature. With increasing temperature from 175 to 180 °C, the SPR peaks become broad and three peaks appear at 355, 410, and 440 nm. The two former peaks are ascribable to SPR bands of 1D Ag nanoparticles; the last one can be assigned to SPR bands of quasi-cubic and quasi-bipyramidal structures.

To confirm morphologies of Ag nanostructures at 180 °C, TEM images of products were measured for bubbling of N$_2$ and air (Figs. 5B and 5D). An outstanding finding is that there is no marked difference in yields of respective products obtained under bubbling air and N$_2$ at 180 °C. On the other hand, it was found that the growth rate of 1D product is much higher than those of cubes, bipyramids, and spheres in the 180–198 °C range for both bubbled gases; growth is especially rapid under bubbling air. Furthermore, the last peak of the cubes and bipyramids disappears at 198 °C, which indicates the yields of cubes, bipyramids, wires, and spheres are much lower under bubbling air in the 180–198 °C range.

Based on the above findings, we proposed the mechanism of the Ag nanostructure formation under bubbling N$_2$ and air (Fig. 6). The reaction process was separated into two stages. The first stage is from room temperature to ca. 180 °C and it need about 16 min to finish this process under oil-bath heating at 500 W; seed nucleation and formation take place.
at this low temperature range. The solubility constant of AgCl in EG is very small at a room
temperature (ca. 20 °C). Therefore, there is little free Cl\(^{-}\) anion existed in the solution and
almost all Cl\(^{-}\) from NaCl is present as small AgCl nanoparticles. These indiscernible AgCl
particles can serve as seeds of Ag anisotropic nanoparticles. With increasing the temperature
from room temperature to 180°C, AgCl is dissolved gradually in EG and much Ag\(^{+}\) and Cl\(^{-}\)
are released to the reaction solution, which supply reducing materials to neutral Ag. In a
separate experiment we have confirmed that Ag nanoparticles are actually produced
directly from AgCl by heating an AgCl solution from room temperature to 180 °C. This
result indicates that AgCl is dissolved and reduced to Ag. It finally provides small Ag
nanoparticles in EG in this temperature region.

![Diagram of proposed mechanism of Ag nanostructures](Fig. 6. Proposed mechanism of Ag nanostructures synthesized from AgNO\(_3\)/NaCl/PVP/EG mixtures using bubbling of N\(_2\) and air.)

In the first stage in Fig. 6, the Cl\(^{-}\) concentration is low so that oxidative etching rates are
slow. Under such conditions, the etching rate is insufficiently high to etch small Ag
particles. Therefore, effects of gas are unimportant, and mixtures of cubes, bipyramids, and
rods are produced in both bubbling of N\(_2\) and air at temperatures less than ca. 180 °C. The
second stage is the high-temperatures from 180 to 198 °C. In this range, the etching rate
increases with the increasing in the concentration of Cl\(^{-}\). Thereby, oxidative etching rates
become so high that small Ag particles can be etched in the presence of O\(_2\). In this range, the
growth rates of Ag seeds also increase considerably: rapid crystal growth and oxidative
etching occur competitively. The relative rate of crystal growth and oxidative etching
strongly depends on shapes of Ag particles. In this condition, the growth rate from
decahedra to 1D products is fast, whereas the etching rates of other products are fast.
Therefore, Ag nanowires are produced in a high yield.

In general, shapes of the final products depend not only on the stability of crystal structures
against etching by Cl\(^{-}\)/O\(_2\) but also the density of Ag\(^{0}\) atoms around the growing nuclei. A
high related ion concentration around the nuclei can create an environment with high
twinning probability for the formation of MTPs from which pentagonal 1D rods and wires
are grown. Thus, five-twinned 1D products are favorable at higher concentration of Ag\(^{+}\)
ions, whereas single crystal cubes are preferentially formed at lower concentration of Ag\(^{+}\)
ions.

In order to further confirm the effect of NaCl in the synthesis of silver nanowires, a series of
experiments were carried out without gas bubbling [28]. First Ag nanostructures were
prepared at various NaCl concentrations from 0 to 0.45 mM. We found that the concentration of NaCl strongly affects the final shapes of products. A low concentration of NaCl (0.12 mM) is in favor of the formation of cubes and bipyramids, whereas a higher concentration of 0.3 mM is the best condition for the formation of NaCl nanowires.

We classified mechanisms for the formation of Ag nanostructures into three cases as shown in Fig. 7, depending on the molar ratios of [NaCl]/[AgNO₃]. Case (a) is [NaCl]/[AgNO₃] = 0. When the NaCl is absent, Ag⁺ ions are reduced to Ag⁰, nucleation occurs, and then the Ag seeds are formed and their growth leads to spherical particles formed randomly. Case (b) is [NaCl]/[AgNO₃] = 1. When equal molar concentrations of AgNO₃ and NaCl are mixed at room temperature, AgCl is formed due to the small solubility constant of AgCl. In this case, AgCl is dissolved as Ag⁺ and Cl⁻ with increasing temperature. After then Ag⁺ ions are reduced to Ag⁰ and nucleation, seed formation, and crystal growth take place. Since the concentration of Ag⁺ ions is low, twinning probability is low. Therefore, single crystal cubes and single-twin bipyramids are produced preferentially. Case (c) is an intermediate between the above two cases: [NaCl]/[AgNO₃] = 0.0065. In this case, although AgCl is formed, a large excess amount of AgNO₃ is present in the solution. The standard electrode potential of AgCl + e⁻ → Ag + Cl⁻ (+0.2233 V vs. SHE) is lower than that of Ag⁺ + e⁻ → Ag (+0.799 V vs. SHE). Under such a condition, most of the Ag⁰ atoms do not arise from AgCl but from free Ag⁺. In this case, major products are five-twinne 1D particles because the concentration of Ag⁺ ions is sufficiently enough to provide a high probability for twinning.

Fig. 7. Possible nucleation and growth mechanisms of Ag nanostructures at different molar ratios of [NaCl]/[AgNO₃].

In the case of the liquid phase method, previous studies on anisotropic growth of Ag nanomaterials have demonstrated that Pt seeds as exotic nuclei play a key role with PVP
served as a capping reagent. Xia et al. have described a soft template assisted solution-phase approach for the production of 1D nanostructures by reducing AgNO$_3$ in the presence of PVP and PtCl$_2$ in EG at a high temperature using oil bath [29]. They have suggested that the formation of the 1D Ag nanostructures proceeds via two steps. The first step involves the formation of Pt nanoparticles with an average diameter of 5 nm by reducing PtCl$_2$ with EG.

$$\text{2HOCH}_2\text{-CH}_2\text{OH} \rightarrow \text{2CH}_3\text{CHO + 2H}_2\text{O} \quad (1)$$

$$\text{2CH}_3\text{CHO+PtCl}_2 \rightarrow \text{CH}_3\text{CO-COCCH}_3 + \text{Pt + 2HCl} \quad (2)$$

At second step, AgNO$_3$ and PVP are added into the reaction system drop-by-drop, leading to the nucleation and growth of Ag nanowires. They thought that the pre-synthesized Pt nanoparticles serve as seeds for the heterogeneous nucleation and growth of silver owing to the close match in crystal structure and lattice constants. Then Ag nanoparticles with diameters of 20-30 nm were created following the nucleation process. Many Ag atoms also nucleated through a homogeneous process and formed critical particles with diameter of 1-5 nm. At high temperature, critical particles progressively disappeared to benefit the growth of large particles via the famous Ostwald ripening [30]. With the assistance of PVP, some of the large particles grow into nanowires with diameters in the range of 30-40 nm. Usually the growth process would continue until all these critical silver particles with diameters less than 5 nm were completely consumed, and only nanowires and larger nanoparticles can survive stably.

Our group have conducted a further detailed study on the real role of Pt seeds as a nucleation agent for the preparation of 1D Ag nanostructures by using the MW-polyol method [23]. To examine effects of Pt seeds and Cl$^-$ anions, a various kind of experiments were carried out. When Pt catalysts were prepared from two different agents, H$_2$PtCl$_6$6H$_2$O and Pt(acac)$_2$, the 1D Ag nanostructures could be easily prepared only by using H$_2$PtCl$_6$6H$_2$O, although Pt seeds could be produced when using either of them. This result might indicate that Pt catalysts probably do not act as seeds for evolution of the 1D Ag nanostructures. In contrast, it is possible for Cl$^-$ ions resulting from H$_2$PtCl$_6$6H$_2$O to play an important role in assisting the formation of the 1D Ag nanostructures. So we used NaCl or KCl as a source of Cl$^-$ ions to elucidate the role of Cl$^-$ ions. We found that nanowires could be prepared when using either of them. In addition, besides the 1D Ag products, the formation of some well-crystallized cubic and bi-pyramid Ag nanocrystals with sharp edges has been found to be related to existence of Cl$^-$ ions. We confirmed that the so-called Pt seeds-mediated process is in fact a salt-mediated polyol process.

### 2.3 Seed-mediated growth approach

Murphy et al. firstly reported the large-scaled preparation of silver nanowires with uniform diameter by seed-mediated growth approach in a rod-like micellar media [31]. In principle, two steps were necessary in order to achieve the formation of nanowires. Firstly, Ag nanoseeds with an average diameter of 4 nm were prepared by chemical reduction of AgNO$_3$ by NaBH$_4$ in the presence of trisodium citrate. Then AgNO$_3$ was reduced by ascorbic acid in the presence of Ag seed obtained in the first step, the micellar template cetyltrimethylammonium bromide (CTAB), and NaOH in order to synthesize nanorods and nanowires with various aspect seed. This seed-mediated growth approach is prone to form silver nanorods and nanowires of controllable aspect ratio.
It is well documented that Ag nanowires were one of the earliest twinned Ag nanostructures reported and now have become an active area of research in Ag nanoparticles. But it was always a great challenge to achieve control over the length and width of Ag nanorods and nanowires. At the same time, silver nanorods and nanowires with pentagonal cross-section have been proposed to come from the evolution of decahedra. Recently, Kitaev et al. synthesized monodisperse size-controlled faceted pentagonal silver nanorods by thermal regrowth of decahedral silver nanoparticle in aqueous solution at 95 °C, using citrate as a reducing agent [32]. Here we will introduce this method although it is a synthesis method of Ag nanorods. Firstly monodisperse decahedral Ag nanoparticles were synthesized by photochemical method and the size of decahedron can be controlled in a larger scale range by regrowth. Then, silver decahedra were added into a temperature-controlled solution and a thermal regrowth was carried out at 95 °C with the presence of PVP with citrate as a reducing agent. Fig. 8 shows the typical SEM images of the resulted monodisperse pentagonal Ag nanorods. These faceted pentagonal rod particles readily self-assemble into densely packed arrays upon drying of their dispersions owing to the excellent monodispersity and good stabilization in aqueous solution. It was found that PVP can improve the yield and stability of Ag nanoparticle, but not absolutely necessary for the shape control. Ag nanorods with various aspect ratio of length to diameter can be achieved by semicontinuous silver addition and the width of nanorods was determined by the size of decahedron. Due to the ease of preparation and excellent shape and size control, this method is well worth further studying and can be extended to the synthesis of Ag nanowires in the future. These nanorods will be attractive for diverse practical applications due to the reliable synthetic approach, high monodispersity, excellent size control.

![SEM images of self-assembled packing of monodisperse pentagonal Ag nanorods.](image)

Before the work of Kitaev et al. [32], silver nanorods and nanowires have also been synthesized in our group using multiple twin decahedron (MTD) of gold as the seed by the MW-polyol method [33]. Because gold and silver have the same FCC crystal structures, and the lattice constants of Au (0.4079 nm) and Ag (0.4086 nm) are very similar, there are many kinds of Au@Ag core-shell structures can be prepared from Au/Ag reagents. The final shape of Ag outer shell was decided by the shape of Au inner core. The Au@Ag core-shell nanostructures were synthesized in two steps. The first step was the synthesis of an Au inner core, and the second step was the preparation of an Ag outer shell including nanorods...
and nanowires. Fortunately, the thin boundary layers of Au@Ag core-shell structures can easily be observed from TEM images, because Au cores and Ag shells appear as clear black and blight contrasts, respectively. Based on the TEM observation of Au@Ag particles prepared at different [Ag]/[Au] molar ratios (Fig. 9) and EDS data, the growth mechanism of Au@Ag nanocrystals overgrown on an MTD Au core was illustrated in Fig. 10. The MTD nanocrystals consist of ten \{111\} facets and crystal growth occurs in two opposite \(<110>\) directions with the same growth rates. Because PVP molecules selectively adsorb on the surface of five rectangular side \{100\} facets and, crystal growth occurs on the exposed active \{111\} facets. Thus Ag shells are continuously overgrown on MTD particles along \(<110>\) directions because active \{111\} facets with a constant total area remain during the crystal growth. During our studies on core-shell nanocrystals, we have found that Ag rods and wires are overgrown on the MTD Au crystals located in the center of the 1-D particles. This result provides the first definite experimental evidence that the previously proposed growth mechanism of 1-D Ag nanorods and nanowires is valid. It was found that optical properties of Au@Ag nanocrystals are different from that of pure Au core and Ag shell nanocrystals, they can be applied to a new optical device.

![Fig. 9. TEM photographs of Au@Ag nanorods and nanowires prepared by addition of various amounts of AgNO₃ to Au cores.](image)

![Fig. 10. Growth mechanism of Au@Ag nanorods and nanowires from the decahedral Au core.](image)
2.4 Seedless and surfactantless wet chemical synthesis

Previous strategies to control the growth of Ag nanowires have involved either softer directing agents, including surfactants or polymers. It is hard work to remove the directing agent from nanowires surface because multiple washings are required. For some sensing applications, the surface-bound residue from the synthesis increases the difficulty of doing chemistry at the surface. Murphy and co-workers reported a method to make crystalline silver nanowires in water, in the absence of a surfactant or polymer to direct nanoparticle growth, and without externally added seed crystallites [34]. The reaction is one in which silver nitrate is reduced to silver metal at 100 °C by sodium citrate in the presence of NaOH. Hydroxide ion concentration was an important factor in determining the morphology of the final product. Ag nanowires prepared by this method is up to 12 microns long. In this synthesis, the citrate plays multiple roles. It not only strongly complexes with the silver ion but it is also responsible for the reduction to silver metal and acts as a capping agent to the silver metal. Although only small amount of hydroxide exists in the reaction solution and hydroxide weakly complexes with the silver ion, but it is enough to interfere with the capping ability of citrate and lead to the formation of Ag nanowires. It is a simple method to prepare nanowires of silver in high yield, with relatively few spherical nanoparticle byproducts. Most importantly, it does not require a surfactant or polymer template, or seeds. This method makes it possible to prepare metallic nanostructures with as “clean” surfaces in water.

2.5 Seedless and surfactant assisted synthesis

Surfactant assisted synthesis is one of the soft-template processes. Murphy et al. have successfully synthesized silver nanorods or nanowires with a rod-like micelle template in CTAB assisted process [31]. During their experiment procedure, seeds are also required in order to achieve the growth of nanorods or nanowires as described in 2.3, so the reaction system becomes complicated. For the surfactant approaches, when the concentration of surfactant is above the critical concentration, micelles with a certain shape will form and act as a soft template. Nanorods and nanowires with controllable aspect ratio are fabricated with the absence of seeds. If the surfactant concentration is too low to form any micelles, it only acts as a capping agent or dispersing agent. Murphy and coworkers also reported the seedless and surfactantless wet chemical synthesis of silver nanowires, in which tri-sodium citrate serves as a capping agent and reducing agent [34] as shown in 2.4. The limitation of surfactantless approach is that it can’t well control the dimensions and morphologies of the product and nanowires obtained with this method are poorly dispersed.

Tian and co-workers developed a seedless surfactant process to synthesize high-quality Ag nanorods and nanowires in large quantities [35]. Silver nitrate is reduced by tri-sodium citrate (Na₃C₆H₅O₇) in the presence of sodium dodecylsulfonate (SDSN). In this process, tri-sodium citrate plays an important role, and SDSN only acts an assisting role as a capping agent in the formation of Ag nanowires. The concentration of SDSN actually used in the experiment process of Ag nanowires is only 1 mM, which is far lower than the critical concentration for the formation of spherical micelles (9.7 mM, 40 °C). Especially, the critical concentration of the micelle formation for SDSN increases with temperature rising. So there are no SDSN micelles formed to serve as a soft template during the whole process of forming nanostructures. The diameters and aspect ratios of Ag nanowires or nanorods can be controlled by changing the concentration of tri-sodium citrate. However, it does not mean that SDSN is unnecessary for
the formation of nanorods or nanowires. Ag nanowires cannot generate under too-low or too-high concentration of SDSN. The key to form Ag nanowires is to well control the tri-sodium citrate concentration for a fixed SDSN concentration.

Fig. 11 shows the proposed schematic illustration for the growth of Ag nanorods and nanowires. At a lower concentration of tri-sodium citrate below 0.2 mM, Ag monomer concentration favors the formation of nanospheres according to Ostwald ripening and small particles dissolve into the solution and deposit on large particles. At a higher concentration of tri-sodium citrate beyond 0.2 mM, a large quantity of monomers is produced in the solution and the growth mode is diffusion-controlled. The monomer concentration in the stagnant solution keeps the solubility of the (110) facet by a rapid growth onto or dissolution from the facet in the assistance of SDSN. It is well documented that the activation energy of the (110) facet is lower than that of (100) and (111) owing to the relative high surface free energies for a FCC structured metal particle. Therefore, monomer particles grow up along <110> directions owing to the strong bonding abilities and chemical reactivities of (110) facet. Thus nanorods are obtained. At higher concentration tri-sodium citrate (>0.8 mM), nanowires with smaller diameter and higher aspect can be formed because of the higher Ag monomer concentration and high velocity of crystal growth.

![Fig. 11. Schematic illustration of the experimental mechanisms to generate spherical, rod- and wire-like nanoparticles.](image)

3. Typical synthetic strategies of Ag nanowires of Coaxial nanocables

In recent years, coaxial nanocable as a new nanostructure has also received great attention because their functions could be further enhanced by fabricating the core and sheath from different materials, which will find use as interconnects in fabricating nanoelectronic devices. Ag-polymer nanocables became a major focus of cable-shaped nanostructures, due to its extremely high electrical conductivity in the bulk and its unusual optical properties depending on the size. It has also been predicted that Ag nanowires with polygonal or circular cross sectional symmetry would exhibit different resonances and a dielectric coating would lead to a red-shift of the SPR peak [36,37]. According to the traditional crystal-growth theory, it is impossible to form Ag nanowires with circular cross-section. Cable-like structures make it possible for the formation of nanowires with expected cross-sections. Then many approaches were developed to achieve Ag nanocables. Xia’s group first reported the preparation of Ag nanocables by directly coating bicrystalline silver nanowires with conformal sheaths of silica through a sol-gel process [38]. Yu et al. [39] introduced a simple large-scale hydrothermal synthesis of flexible nanocables with silver as
cores and cross-linked poly(vinyl alcohol) (PVA) as shells. In a typical procedure, a clear solution containing 0.06 mM AgNO$_3$ and 5 mL PVA (3 wt %) solution was added into Teflon-lined stainless steel autoclave, which was sealed and maintained at 160 °C for 36 or 72 h and then cooled to room temperature naturally. The resulting product is composed of flexible fibers with a diameter of 0.7-4 µm and length up to 100 µm (Fig. 12a). All these silver nanowires show a composite structure of a smooth core and a surrounding sheath (Figs. 12b-12e). At the same time, it is well distinguished between surrounding polymer and inner core. The shell thickness of the obtained nanocables is decided by the reaction time and the temperature can also affect the thickness of the shell. It is well worth noting that PVA cannot become cross-linked in the absence AgNO$_3$ after a hydrothermal treatment and keep other parameters constant, which indicate that AgNO$_3$ is essential for the formation of cables. In fact, AgNO$_3$ acts as a catalyst for oxidation-reduction reactions and PVA can be oxidized by AgNO$_3$ at 160 °C into cross-linked PVA. It is promising to extend this method to the synthesis of other metal-polymer coaxial nanocables.

Li et al. achieved the synthesis of cylindrical Ag nanowires by using an amorphous coating to modify the growth behaviour of Ag nanowires [40]. In their synthesis, Ag$^+$ ions are reduced by glucose under hydrothermal conditions with the presence of PVP in the temperature range of 140-180 °C. These resulted Ag nanowires at 180 °C show a narrow diameter distribution of 16 to 24 nm and the lengths usually reach tens of micrometers. Such slim nanowires show excellent flexibility, which indicates good machinability for future nanodevice fabrication. Further insight to the structure was obtained by high-resolution TEM, which showed Ag nanowires are coated by a multilayer sheath and cable-like structures are created. The sheath should be composed of carbonaceous layers according to previous study that carbonization of glucose could take place under similar conditions. For the formation of Ag@C nanocables, they proposed that Ag nanowires first grew up and then carbonaceous growth units stick on the edges of polygonal crystals owing to the higher
surface tension and more dangling bonds. At a low reaction temperature of 140 °C, only well-crystallized pentagonal nanowires were obtained. This reason can be attributed to that carbonization process is significantly delayed. In summary, high-purity cylindrical Ag nanocables can be selectively prepared through kinetic control of the hydrothermal conditions.

4. Conclusion

Fabrication of silver nanowires has a special significance in many applications, since the optical properties of silver show superior properties compared to that of any other metals with respect to the losses in the localized surface plasmon resonance, or in the propagation of the one-dimensional surface plasmons. The fact that silver nanowires are excellent conductors of both electrons and photons opens up intriguing possibilities for electro-optical devices. Due to high electrical conductivity, silver nanowires are also promising materials as ultra large-scale circuits and quantum components, as well as for electron field emission sources in FEDs (field emission displays).

This article gave a simple introduction to the synthesis methods and growth mechanisms of Ag nanowires, which were developed in the recent ten years by many research groups. Silver nanowires as the most typical metal nanowires has become an important branch of metal nanowires, and these methods used for the synthesis of Ag nanowires can supply reference for the synthesis of other metal nanowires. Every approach involved in this article has the merit and disadvantage, but all of them can give us some elicitation which will benefit to explore new strategies in the future.

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6. References


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This book describes nanowires fabrication and their potential applications, both as standing alone or complementing carbon nanotubes and polymers. Understanding the design and working principles of nanowires described here, requires a multidisciplinary background of physics, chemistry, materials science, electrical and optoelectronics engineering, bioengineering, etc. This book is organized in eighteen chapters. In the first chapters, some considerations concerning the preparation of metallic and semiconductor nanowires are presented. Then, combinations of nanowires and carbon nanotubes are described and their properties connected with possible applications. After that, some polymer nanowires single or complementing metallic nanowires are reported. A new family of nanowires, the photoferroelectric ones, is presented in connection with their possible applications in non-volatile memory devices. Finally, some applications of nanowires in Magnetic Resonance Imaging, photoluminescence, light sensing and field-effect transistors are described. The book offers new insights, solutions and ideas for the design of efficient nanowires and applications. While not pretending to be comprehensive, its wide coverage might be appropriate not only for researchers but also for experienced technical professionals.

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