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Preparation of Silver Nanowires via a Rapid, Scalable and

Green Pathway

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Rapid synthesis of silver nanowires (Ag NWs) with high quality and a broad processing window is challenging because of the low selectivity of the formation of multiply twinned particles at the nucleation stage for subsequent Ag NWs growth. Herein we report a systematic study of the water-involved heterogeneous nucleation of Ag NWs with high rate (less than 20 min) in a simple and scalable preparation method. Using glycerol as a reducing agent and a solvent with a high boiling point, the reaction is rapidly heated to 210 °C in air to synthesize Ag NWs with a very high yield in gram level. It is noted that the addition of a small dose of water plays a key role for obtaining highly pure Ag NWs in high yield, and the optimal water/glycerol ratio is 0.25%. After investigating a series of forming factors including reaction temperature and dose of catalysts, the formation kinetics and mechanism of the Ag NWs are proposed. Compared to other preparation methods, our strategy is simple and reproducible. These Ag NWs show a strong Raman enhancement effect for organic molecules on their surface.

KEY WORDS: Silver nanowires; Synthesis kinetics; Surface enhanced Raman scattering

1. Introduction

One-dimensional (1-D) metallic nanostructures have attracted materials scientists for years due to their unique electronic, optical, thermal, and catalytic properties with dimensionality and size confinement^[1-3]. Among such materials, silver nanowires (Ag NWs) have been intensively studied due to their potential applications in plasmonic fibers, photonic crystals, electronic interconnectors, transparent electrodes, cell probes, and so on^[4-6]. Considering these promising applications, it is critically important to develop efficient and scalable synthesis of NWs and to have more detailed understanding about the formation kinetics.

A number of preparation approaches have been developed to synthesis high quality Ag NWs with adjustable configurations, including the top-down^[5] and bottom-up methods^[7–9]. In term

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of cost, yield and simplicity, liquid phase growth approaches seem promising. For example, Fievet et al.^[10] introduced the polyvinylpyrrolidone (PVP) mediated AgNO3 reduction process by polyol. Xia et al.^[2] and Sun et al.^[7] improved the method and obtained Ag NWs with high aspect ratios at a well-defined reactant addition rate in a dried ethylene glycol system. The AgNO₃ and the PVP solutions were simultaneously added into the hot ethylene glycol solution using a two-channel syringe pump at a constant temperature. Ethylene glycol acted as both solvent and reducing agent, and Ag NWs were generated via a self-seeding manner. In that scenario, low precursor concentrations and slow addition rates are essential to form multiply twinned particles (MTPs) at the initial stage (nucleation) of the reduction process and serve as seeds for the subsequent growth of the Ag NWs^[11,12]. As a consequence, liquid phase syntheses of Ag NWs have been regarded as the most promising method by virtue of their various advantages such as homogeneous reaction, wide range of applicable solvents, simple monitoring technology, and low cost.

The prior studies suggest that a trace amount of salts is effective in improving the quality of the resulting materials. For example, Fe(II) and Fe(III) salts have been shown to facilitate the growth of 1-D Pt and Ag nanostructures^[13]. Cu(I)/Cu(II) and Na₂S^[14,15] have been used as additives to modify the growth of

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the final product. In those cases, Ag NWs were produced in the presence of PVP as surfactant and argon as shielding gas. As this control agent reaches a high concentration, the 1-D product would dominate the product rather than the 0-D nanoparticles. During the initial stage of the reaction for nucleation, the formation of Ag₂S colloid induces the deposition of Ag atoms, and the Ag₂S/Ag binary seeds serve as auto-catalysts in Ag reduction. Therefore, overall, various amounts of stainless steel or Na₂S, Fe(II)/Fe(III) containing salts, Cu(I)/Cu(II) salts could lead to the formation of Ag NWs of uniform size and morphology.

There have been discussions of the 1-D growth mechanism for Ag NWs by Lofton and Sigmund^[16]. Typically, for the nucleation process, the appropriate seed crystals (such as MTPs of decahedral shape, bound by ten (111) facets) must be preferentially generated in the solution. For the subsequent growth process of the NWs the deposition of Ag atoms needs to be precisely controlled on the (111) facet for the preferable crystal orientation directions. In the first stage (nucleation), the formation of the twinned nanostructure is favorable due to the surface energy minimization once the particle size has reached a critical value^[16]. MTPs can be produced conveniently by the wet chemical method because the twin boundaries on their surfaces have the highest energy, which drives the diffusion of Ag atoms onto those sites. This driving force leads to the uniaxial elongation of the MTPs. The PVP facilitates this uniaxial elongation by preferential passivation on the (100) side surfaces of the NWs, so that the subsequent reduction of Ag atoms is mainly located along the (111) faceted ends^[17]. As the reduction of Ag cation continues, the MTPs can grow into Ag NWs. As well, Wiley et al.^[18] elucidated that the Ag NW growth mechanism involves the oxidative etching process in the presence of chloride. As shown in their experimental observations, Ag NWs grow along the [100] direction and the deposition of Ag atoms occurs on the edges of the (111) facet. Benefiting from the initial MTP structures, the seeds develop into 1-D nanowires under a controllable addition rate of both Ag cation and PVP. Further to those studies, Tang et al.^[19] developed a rapid synthesis of Ag NWs and described the air-assisted polyol method of synthesizing Ag NWs within 20 min, based on a condition of controlled air bubbling. In Tang's method, the temperature was rapidly raised to about 200 °C within 20 min, so that the reaction process was much accelerated. The key step for the method is the rate of air bubbling into the system, which can produce high quality Ag NWs with uniform size and shape. Guo et al.^[20] and Tang et al.^[21] demonstrated an aerobic preparation method involving a

microwave-assisted condition, suggesting a rapid preparation method.

Water is thought to be one of the impurities relative to various polyol reactants in polyol synthesis of Ag NWs. However, water as a polar ionic solvent is critical to the formation of Ag NWs considering the strong interaction between –OH with Ag, yet the influence of water to the reaction is still absent. In this study, we aim to give a detailed elucidation about the processing windows of the preparation of Ag NWs in large scale (by grams) including the influence of water content, catalyst species and the reaction status at different temperatures for a rapid synthesis scheme. The results suggest that appropriate temperature and time are crucial to produce Ag NWs, whereas water/glycerol ratio influences the diameter and length of the nanowires. We also evaluated the resulted nanowires as the substrate for surface enhanced Raman spectroscopy (SERS) to detect organic molecules, e.g. Rhodamine 6G.

2. Experimental

2.1. Materials

All chemicals (silver nitrate (AgNO₃), PVP (Mw = 55,000 g/mol), glycerol, sodium chloride (NaCl), potassium chloride (KCl), potassium fluoride (KF), potassium bromide (KBr), potassium iodide (KI), lithium chloride (LiCl), magnesium chloride (MgCl₂) and calcium chloride (CaCl₂), were obtained from Aldrich without further treatment.

2.2. Preparation of Ag NWs

A series of experiments were conducted to understand the synthesis process, and the conditions are listed in Table 1. In a typical procedure, 190 mL of glycerol solution containing 6 g of PVP was mixed and gently heated to 80 °C until all PVP is dissolved, and cooled to room temperature, then added into a round-bottom flask. AgNO₃ powder (1.58 g) was then added to the solution with vigorous stirring until the powder was fully dissolved. Subsequently, 58.5 mg of NaCl (5 mmol/L in total solution) was dissolved in 0.5 mL H₂O and added into 10 mL of glycerol (as for the control experiment, the other metal halide control agent was added in the same methods). The latter was added into the flask and the reaction temperature of the mixture was rapidly raised to 210 °C within 20 min, roughly 8 °C/min

Table 1 Sequence of reaction conditions

No.	Water (mL)	Gas environment	Control agent species	Product	Shown in figure
1	0.5	Air	NaCl (5 mmol/L)	Ag NWs	1
2	0.5	Air	NaCl (or KCl) (5 mmol/L)	Ag NWs	4(f)
3	0	Air	NaCl (5 mmol/L)	Ag NWs + NPs	4(a)
4	0	N_2	NaCl (5 mmol/L)	Ag NWs + NPs	4(b)
5	0.5	Air	KF (5 mmol/L)	Ag NPs	5(a)
6	0.5	Air	KBr (5 mmol/L)	Ag NPs	5(b)
7	0.5	Air	KI (5 mmol/L)	Ag NWs	5(c)
8	0.5	Air	LiCl (5 mmol/L)	Ag $NWs + NPs$	5(d)
9	0.5	Air	MgCl ₂ (2.5 mmol/L)	Ag NWs + NPs	5(e)
10	0.5	Air	$CaCl_2$ (2.5 mmol/L)	Ag NWs + NPs	5(f)
11	1.0	Air	NaCl (5 mmol/L)	Ag NWs + NPs	4(c)
12	1.5	Air	NaCl (5 mmol/L)	Ag NWs + NPs	4(d)
13	0*	Air	NaCl (5 mmol/L)	Ag NPs	4(e)

Notes: NW-nanowire; NP-nanoparticle; *-0.5 mL ethanol is added instead of water.



Fig. 1 UV-vis absorption spectra of the Ag nanomaterials at different formation stage, using the reaction condition No. 1 as shown in Table 1 under the heating rate of about 8 °C/min.

with a heating mantle equipped with a PTFE paddle stirrer (at 50 r/min) in the aerobic condition. When the reaction was stopped and the flask cooled down to room temperature, the deionized water was added into the flask by a 1:1 volume ratio, and then the mixture was centrifuged at 8000 r/min until all visible products were collected. The transparent supernatant was discarded and the as-obtained Ag NWs were washed by water three times to remove the PVP residue. Studies of the effect of water concentration and metal cation species were conducted.

2.3. Preparation of Ag NWs

Scanning electron microscopy (SEM, JEOL 6300) at 15 kV was used to study the morphology of the reaction products. Transmission electron microscopy (TEM, JEOL 2010) at 200 kV was used to analyze the Ag NWs in more detail. UV-vis analysis was performed on a Shimadzu UV-2450 spectroscope. Powder X-ray diffraction (XRD) spectra of the Ag NW films were obtained using a PANalytical X-ray diffractometer, Model X'pert

Pro. Raman spectra of Ag samples were obtained using a Renishaw Invia Reflex equipped with a 514 nm laser. A silicon wafer was used as the sample substrate for the measurements; analysis was performed immediately after the deposition of the Rhodamine 6G aqueous solution onto the Ag NW film.

3. Results and Discussion

3.1. Temperature

During the reaction process, the color of the solution turns from pale white to light brown, red, dark gray, and eventually gray-green (at about 200 °C). UV-vis absorption spectra of the Ag NWs in the aqueous solution were used to understand the kinetics of the formation of Ag NWs (Fig. 1). When the reaction temperature is lower than 180 °C, the absorption peak at 410 nm gradually decreases with the rise of temperature, which is consistent with the surface plasmon resonance (SPR) signals related to the formation of Ag nanoparticles and short nanorods (aspect ratio less than 10)^[22]. Further raising the temperature results in a bump over 500 nm. The red shift of this bump suggests the growth of Ag nanorods. When the temperature reaches 190 °C, new peaks appear at 350 and 380 nm, which are attributed to the Ag NWs^[23]. When the temperature is higher than 190 °C, the intensity of peaks becomes higher with increasing temperature, but it has no significant change in the shape of the two peaks. As a matter of fact, the Ag NWs begin to grow at near 190 °C, and then after about 5 min, when the temperature reaches 210 °C, the reaction is stopped.

To further study the influence of temperature, the reaction products at different formation stages were investigated by TEM, which are shown in Fig. 2. Fig. 2(a) shows the solid product obtained at 140 $^{\circ}$ C after centrifugation in water to eliminate the soluble salts and surfactant. Some cloudy matter is related to the insoluble amorphous AgCl. Further raising the reaction temperature to 170 $^{\circ}$ C results in the formation of some Ag



Fig. 2 TEM images of the product at different reaction temperatures in condition No. 1 listed in Table 1: (a) 140 °C, (b) 170 °C, (c) 190 °C, (d) 210 °C, (e) detailed morphology of the Ag NWs (f) detailed morphology of the Ag NWs (inset: SAED pattern of a single tip of Ag NW^[24]).

nanoparticles and short nanorods of ~2 µm in length (Fig. 2(b)). When the temperature is raised to 190 °C, the nanoparticles gradually diminish and the length of the nanorods increases to about 5 µm (Fig. 2(c)). When the temperature finally reaches 210 °C, most of nanoparticles disappear and NWs are the predominant product, with the average length of about 10 µm (Fig. 2(d)). Prolonging the reaction time to 30 min at this temperature produces no obvious increase in NW length, while agglomerates were observed in the reaction solution. The selected area electron diffraction (SAED) pattern obtained by focusing the electron beam onto the NW samples can be indexed to Ag fcc structure with a lattice constant of 0.408 nm, which is identical to the XRD analysis. Therefore, this synthesis method provides Ag NWs growing along the [111] direction of single crystal.

3.2. Reducing agent

Ethylene glycol (EG) has been predominantly used for the reduction of Ag cations in the polyol process^[24]. Herein, the glycerol was instead adopted as the reducing agent for the following reasons, (i) as a common polyol solvent, it has a much higher boiling point (290 °C) than EG (197 °C) and propylene glycol (188 °C), so that the reaction temperature can be raised to over 200 °C; (ii) glycerol has a higher hydroxyl content ratio since it has three hydroxyl groups. These two features endow glycerol with a higher reducing ability for Ag cation, which leads to a faster reaction speed; (iii) glycerol is safer to human health.

As the reaction medium, however, glycerol has high viscosity, which decreases the diffusion coefficients of ions (e.g., Ag⁺ or Cl⁻). Therefore, high reaction temperature is needed to increase the solubility and diffusion coefficient of ions. Fig. 3(a) shows an SEM image of the product obtained after reacting for 20 min at 210 °C. This image shows that the product is predominantly NWs about 10 μ m in length, which are similar to those synthesized in EG^[7]. The product contains only a small amount of nanoparticles (NPs). The XRD patterns (Fig. 3(b)) suggest that metallic Ag with fcc structure and high crystallinity is successfully produced through the reaction. The peaks at 38.2°, 44.3°, and 64.4° are assigned to the diffraction from the (111), (220), and (200) planes of Ag, respectively^[24], which is consistent with the literature (JCPDS card number 87-0717).

3.3. Water and oxygen

Generally, for the commercial available polyol solvent with high polarity and boiling points (e.g. glycerol and ethylene glycol), water is difficult to be totally eliminated. Yet in this study, water content was found to be critical to the formation mechanism of Ag NWs. To evaluate the catalytic ability of both water and oxygen in our reaction windows, the control experiments were carried out and the resulting products were analyzed by SEM. All these control experiments followed the same reaction temperature profile of increasing from 25 to 210 °C within 20 min. Because glycerol was vacuum-distilled prior to its use in the synthesis of Ag NWs and dried compressed air was connected to the reaction batch, it was supposed that there was no water's contribution for the results, as shown in Fig. 4(a). Only parts of the solid products contain nanorods and short NWs, most of others are nanoparticles. Fig. 4(b) shows the image of the solid product when neither water nor air was introduced to the system. Instead, high-purity (>99.999%) nitrogen was purged into the reaction vessel prior to the reaction and the gas pressure was maintained near 101.325 kPa(1 atm) during the reaction. Here, a predominant amount of Ag nanocubes and very few nanorods can be observed.

To evaluate the effectiveness of adding trace amount of water, control experiments were performed by increasing the water content. The water/glycerol ratio was doubled (0.5% in Fig. 4(c))and tripled (0.75% in Fig. 4(d)) as the control sample, and the results suggest lower yields of Ag NWs. As well, a control experiment was conducted by replacing water with ethanol. As shown in Fig. 4(e), when the same volume of ethanol was added to the reaction system which used the distilled glycerol as the solvent (no water), only Ag NPs were obtained. In comparison, in Fig. 4(f), an SEM overview image of the reaction product of adding water in aerobic condition, Ag NWs dominates the product. It should also be mentioned that using KCl as the catalyst also resulted in high yield Ag NWs. We thus suppose that as a typical ionic compound and an excellent thermal conductor, water (together with oxygen) plays a subtle role (i) to effectively improve the charge transfer process involved in the growth of silver on the (110) facet; and (ii) to promote the homogenization of the reaction process, and this is especially useful for large scale production of high quality Ag NWs.

3.4. Metal halide control agent

Further to the evaluation of using sodium chloride (NaCl) as the metal halide control agent, control experiments were performed using other alkaline and alkaline earth metal halides. Fig. 5 shows a series of SEM images of the reaction products based on different catalyst species. Fig. 5(a) shows the product of using KF instead of NaCl, only Ag nanoparticles and a small



Fig. 3 (a) SEM image of Ag NWs prepared at 210 °C for 20 min, (b) XRD pattern of the sample of Ag NWs^[24], (c) higher magnification SEM image of Ag NWs prepared at 210 °C for 20 min.



Fig. 4 SEM images of Ag NWs produced in different conditions: (a) vacuum-distilled glycerol with no water, (b) vacuum-distilled glycerol without water or oxygen (N₂ purged), (c) doubled water/glycerol ratio (0.5%), (d) tripled water/glycerol ratio (0.75%), (e) ethanol instead of water as the additive, (f) water (0.25%) and air.

amount of nanorods. Fig. 5(b) shows the image of the product of using KBr, where nanoparticles are the only product. Fig. 5(c) shows the product image of using KI as the control agent, which shows both Ag NWs and nanoparticles. Using LiCl, MgCl₂, or CaCl₂ as the control agent does not give a high yield of Ag NWs, as shown in Fig. 5(d-f). Therefore, NaCl or KCl is the best for AgNW synthesis.

3.5. Formation kinetics

Generally, nucleation of metal nanoclusters in solutions is greatly influenced by the properties of the solvent^[25]. The reduction of metal cations in non-aqueous solvents often encounters obstacles such as low solubility and low thermal conductance; moreover, the transfer of electrons between the



Fig. 5 Products of reactions using different catalysts: (a) KF, (b) KBr, (c) KI, (d) LiCl, (e) MgCl₂, (f) CaCl₂.



Fig. 6 Schematic illustration of the reaction kinetics of the Ag NWs.

reacting species tends to be easier in polar solvents than the nonpolar ones. In the case of Ag NWs preparations, it is noted that glycerol has higher polarity than EG and the introduction of water further improves polarity of the reaction system. The presence of a trace amount of water probably promotes the proton hopping on the surface of the materials, which can facilitate the charge transfer process^[26]. The improved polarity and the higher temperature inevitably accelerate the reaction speed and enhance the Ostwald ripening process^[27], which result in effective and rapid production of thermodynamically favorable nanocrystals. Meanwhile, as a polar ionic molecule, water improves the solubility of both Ag⁺ and Cl⁻, accelerating the formation of AgCl clusters, which is a critical stage in the formation of Ag nanocrystals^[2]. The addition of too much water (e.g. conditions No. 11 and 12, Table 1), however, results in lower production yield of Ag NWs (as shown in Fig. 5(c)). This phenomenon may be ascribed to the burst of steam bubbles which disturbs the micelle stability and the high ionic concentration changes the nucleation mechanism^[16]. This suggests that the appropriate water concentration influences not only solubility and the Ostwald ripening process but also the interaction between the crystal facets and the capping agent (PVP).

As inferred from the in-situ UV-vis spectra and TEM images at different formation stages in Figs. 1 and 2, when the temperature is gradually increased, Ag cations are reduced to Ag atoms and join together to form crystal nuclei and then grains. The freshly formed crystals grow and take various shapes such as multiple twinned, single twinned and single-crystal shapes due to the non-thermodynamic process. Further rising the temperature results in recrystallization of the large shapes through the Ostwald ripening process^[27]. Finally, most of the large Ag nanoparticles grow into rod-shaped anisotropic nanostructures as both the number and length of Ag NWs increase along with the duration of the reaction. The suggested mechanism follows Fig. 6. The Ag cations are first distributed in glycerol with the presence of Cl⁻. Then as the temperature increases, they become fluctuating structures including some amorphous AgCl and Ag seeds. The capping agent (PVP) interacts with the Ag surface through chemisorption and guides the subsequent growth of Ag NPs. Considering the much stronger interaction between the (100) facet of Ag metal and capping agent, the ends of the Ag nanorods ((111) facets) tend to grow much more quickly, resulting in the transformation of the nanorods into Ag NWs^[19]. Moreover, the (111) facet is the most densely packed and energetically the most favorable surface for fcc Ag. Meanwhile, Ag nanoparticles with different morphologies are also present due to

the different growth velocity of various crystal planes for the seeds of Ag. Most of the Ag nanoparticles are inhibited by selective etching with the presence of Cl^- , H_2O and oxygen. A small number of other morphologies of the nano-Ag can also be observed in the products, due to the different growth mechanisms of various Ag seed crystallites generated at the beginning of the reaction.

3.6. SERS of Ag NWs

To evaluate the feasibility of application of the Ag NWs, SERS analysis was performed. Ag NW substrates for the SERS measurements were prepared by soaking them in Rhodamine 6G (R6G) aqueous solutions of 10^{-8} , 10^{-7} , and 10^{-6} mol/L for sufficient time, respectively. The Ag NW substrates were washed by DI water, and then blown by N_2 gas. Fig. 7 shows the SERS spectra in a range of 500–2000 cm⁻¹. The typical SERS signals of R6G on the Ag NW substrates can be observed clearly and the detailed assignment of the peaks is similar to previous reports, including the peaks at 1646 cm⁻¹ (totally symmetric modes of in-plane C-C stretching vibrations), 1596 cm⁻¹ (totally symmetric modes of in-plane C–C stretching vibrations), 1560 cm^{-1} (totally symmetric modes of in-plane C-C stretching vibrations), 1356 cm^{-1} (totally symmetric modes of in-plane C–C stretching vibrations), and 614 cm^{-1} (in-plane bending vibration)^[28]. The SERS enhancement of the samples is attributed to the long-range electromagnetic effect, which may related to the sharp tips and the noncircular cross-sections of the Ag NWs^[6]. The signal intensities are enhanced with increasing concentration of the solution.



Fig. 7 Raman analysis of the Rhodamine 6G samples with different concentrations on the Ag nanowire sample surface.

4. Conclusion

This work proposed an environmentally benign, highly effective, and rapid way of synthesizing Ag NWs. Through a water-assisted glycerol based reduction process, the Ag NWs with diameter of 60-90 nm and length of 8-12 µm in surprisingly high yield without any product separation step were prepared. For the first time, the formation kinetics of a waterinvolved rapid preparation of Ag NWs was systematically investigated. The in-situ UV-vis spectroscopy observing result suggested that choosing a higher reaction temperature was beneficial. It was confirmed that water was an efficient catalyst and 0.25% of water/glycerol ratio was an optimal condition. Moreover, using NaCl or KCl as the control agent led to the production of high quality Ag NWs. Meanwhile, it was noted that when using potassium salts as the control agent, chloride was superior to fluoride, bromide and iodide. The Ag NWs obtained through our method showed a strong SERS effect to R6G molecules. We also envisaged that this work may contribute to the design and development of Ag NWs of greater length and superior homogeneity in mass production with low cost.

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