High-Concentration Preparation of Silver Nanowires: Restraining *in Situ* Nitric Acidic Etching by Steel-Assisted Polyol Method

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A steel-assisted polyol method has been proposed for the preparation of Ag nanowires (AgNWs) at high $AgNO_3$ concentrations of up to 0.5 M. The average diameter of products could be adjusted from approximately 100 to 300 nm by increasing the synthetic concentration. It was found that *in situ* nitric acidic etching was a fatal factor for the stability of the multiply twinned particles (MTPs), which were the seeds of AgNWs in the polyol synthesis system. The introduction of stainless steel could effectively consume the *in situ* generated nitric acid through a corrosion reaction between them, hence enabling the survival of MTPs for the consequent growth of AgNWs.

Introduction

One dimensional (1D) nanostructures of silver with well-defined aspect ratios and high crystallinity have been attracting considerable interest owing to their exhibiting size-dependent mechanical, plasmonic, optical, and chemical properties, as well as the highest electrical or thermal conductivities of all metals.[1] On the basis of these characteristics, Ag nanowires (AgNWs) are of great importance for applications in shape memory materials, plasmonic fibers, photonic crystals, and electrical interconnectors, and also in molecular sensing using surface-enhanced Raman spectroscopy and metal-enhanced fluorescence.[2]

A variety of approaches have been extensively exploited for the preparation of AgNWs on the basis of either a top-down[3] (e.g., electronic-beam or atomic-force lithography) or bottom-up[4] (e.g., template-assisted electrochemical deposition and wet chemical synthesis) strategy. The polyol synthesis of AgNWs was originally introduced by Figlarz and co-workers[5] through the reduction of silver nitrate with ethylene glycol (EG) in the presence of platinum seeds and the organic dispersant of polyvinyl-pyrrolidone (PVP). Xia and co-workers[6] improved the polyol method to obtain AgNWs with higher aspect ratios and discovered the dispensability of the platinum seeds. Nevertheless, in their self-seeding polyol method, the concentration of $AgNO_3$ in the reaction mixture had to be lower than *ca.* 27 mM for the synthesis of AgNWs as the major product,[7] and the slow addition of reactants was necessary.[6a] It was also found by Lofton and Sigmund[8] that the success of synthesis was highly dependent on the order and the rate of reactants addition, hence the complexity of manipulation. Consequently, a facile method capable of massively synthesizing AgNWs with high aspect ratios is strongly desired to provide both quantitative and qualitative support for their application in commercial areas, such as catalysis, electrically conductive adhesion,

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electrostatic dissipation, and electromagnetic interference shielding.[9,10] The availability of AgNWs in large quantities makes a premise for the preparation of thermal, electrical, and other functional composite materials superior to carbon nanotube composite materials.[10,11]

Herein, the authors report a steel-assisted polyol (SAP) method to synthesize AgNWs at high synthetic concentrations. By this method, AgNWs could be obtained as the major product even when the concentration of $AgNO_3$ in the reaction system reached as high as 500 mM, and thereby the output per unit volume was greatly multiplied. Meanwhile, the mechanism for the high-concentration synthesis of silver nanostructures was also explored. It was revealed that *in situ* nitric acidic etching was responsible for the failure of the current polyol method to produce AgNWs at high synthetic concentrations. The SAP method could successfully overcome this obstacle by introducing stainless steel to facilitate the decomposition of the *in situ* generated nitric acid, thus ensuring the mass production of AgNWs for large-scale applications.

Experimental Section

Chemicals and Materials. $AgNO_3$, EG, and PVP (Mw $\approx$ 55 000) were purchased from Shanghai Chemical Reagent Company. All chemicals were used as received without further purification. The stainless steel (Grad 301) grids were obtained from Baosteel Group Corporation and were cut into small pieces before being used. The stainless steel's composition was Si = 1.05%, Mn = 1.05%, Cr = 17.47%, Ni = 7.18%, and Fe = 73.25%, detected by energy dispersive X-ray (EDX) spectroscopy.

Preparation of AgNWs. The typical synthesis of AgNWs by the SAP method involved the following steps. First, 10 mL of $AgNO_3$ solution (0.3 M in EG) and 10 mL of PVP solution (0.45 M in EG, calculated in terms of the repeating unit), together with several small pieces of stainless steel grids (at least 0.5 g), were added into a 100 mL two-necked flask with an air condenser. The mixture was maintained at 120 °C in an oil bath for about 30 min and then was heated up to 140 °C and kept at this temperature for at least 1 h until $AgNO_3$ was completely reduced. The solution finally appeared gray with silvery white stripes (see Figure S1, Supporting Information). Throughout the entire process, the reaction solution was stirred and bubbled with an air flow generated from a mini-sized air pump. The flow rate should be very slow ($\sim$50 sccm in this case) or it will decrease the temperature of the solution. After removing the stainless steel pieces, the solution was centrifuged at 12 000 rpm for 20 min to ensure the complete collection of products and then washed with ethanol and centrifuged three times to remove the EG and PVP on the surface of the products. The final products were preserved in ethanol for further characterization. After drying, the weight of the product was about 0.32 g, which was consistent with the amount of silver source material. This suggested that all of the silver ions were reduced and all Ag products could be collected by this process.

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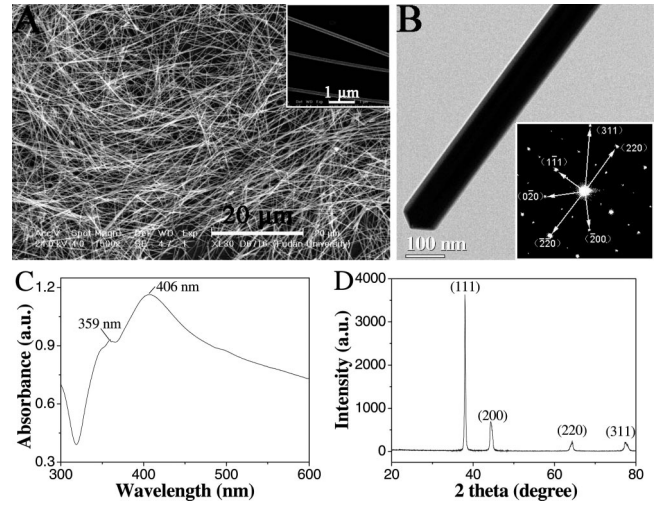

Figure 1. (A) SEM images of AgNWs prepared from $AgNO_3$ (150 mM)/PVP (225 mM)/EG through the SAP method. (B) TEM image and the SAED pattern (inset) of a single AgNW. (C) UV/vis absorption spectrum and (D) powder XRD pattern of AgNWs.

Characterization. Scanning electron microscopy (SEM) and EDX analysis results were obtained on a Philips XL 30 instrument. The transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2010 instrument. In preparing the samples, the products without further purification were well suspended in the ethanol by ultrasonic dispersion. Then, the ethanol suspensions of the products were dropped on the glass substrate for SEM, on the carbon conductive adhesive tape for EDX, and on copper grids coated with amorphous carbon film for TEM. The powder X-ray diffraction (XRD) pattern was taken on a Rigaku D/MAX-rB diffractometer with Cu Kα radiation at 40 kV and 60 mA. The sample was dried under at 60 °C for 24 h before characterization. The ultraviolet/visible (UV/vis) absorption spectrum was obtained on Shimadzu UV 2450 instruments using a quartz cell with 1 cm optical path, and the solution of sample was diluted with ethanol.

Results

Preparation and Characterization of AgNWs. It has been reported that the low synthetic concentration and the slow addition rate of reactants were essential for the synthesis of AgNWs in the conventional polyol synthesis. Silver nanoparticles were the predominant product at concentrations of $AgNO_3$ over 27 mM.[7] In the SAP method, however, AgNWs could be prepared at much higher concentrations of $AgNO_3$. Figure 1A shows the typical SEM images of the sample synthesized at a $AgNO_3$ concentration of 150 mM, in which the nanowires with a mean diameter of ca. 120 nm, lengths of tens of micrometers, and aspect ratios of up to several hundreds (e.g., $\sim$500) can be observed. The curvature of some nanowires implies their nanomechanical bending behaviors. From the SEM image, the estimated yield of 1D nanostructures in the products is >85 wt %. The TEM image in Figure 1B and the selected area electron diffraction (SAED) pattern (inset, Figure 1B) with two sets of spots indicate their bicrystalline structure. The UV/vis absorption spectrum (Figure 1C) of AgNWs presents two absorption peaks at 359 and 406 nm, which are attributed to the plasmon response of bulk silver and the transverse plasmon mode of long AgNWs, respectively.[6a] The powder XRD pattern

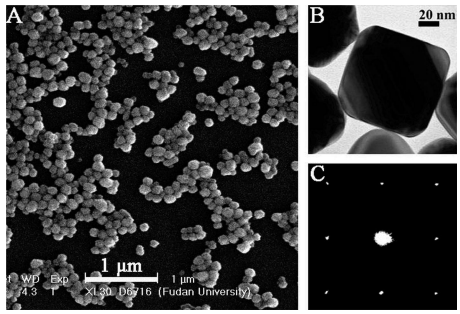

Figure 2. (A) SEM and (B) TEM images of a sample prepared under the same conditions of Figure 1 but without the introduction of stainless steel and bubbled air. (C) SAED pattern recorded by directing the electron beam perpendicular to the (100) facet of a truncated nanocube. The single-crystal structure of products indicates that they did not grow from twinned crystal seeds.

(Figure 1D) of the sample shows that the as-synthesized AgNWs can be indexed to the face-centered-cubic phase belonging to the space group *Fm3m* (225) (JCPDS file No. 04-0783). According to the XRD pattern of Figure 1D, the calculated lattice constant is 4.096 Å, very close to the reported value of 4.086 Å. And, the EDX spectrum shows that no impurities exist in the products (Figure S2, Supporting Information).

As a comparison, an experiment without the addition of stainless steel was carried out under the same conditions as in Figure 1 (a $AgNO_3$ concentration of 150 mM). Figure 2 shows the product morphology and SAED pattern of a typical product. Silver nanoparticles were the predominant product in the steel-absent system, which was very similar to that of previously reported polyol synthesis.[7] Another experiment was also carried out by substituting stainless steel with iron. It was found that irregular Ag particles were obtained as a result of the replacement reaction between Ag^+ and Fe. From the above experiments, a conclusion can be drawn that stainless steel with appropriate reactivity is critical for the formation of AgNWs at high synthetic concentrations.

AgNWs with Various Diameters. To investigate the applicability of the SAP method for the AgNWs synthesis at high concentrations, the experiments were carried out under the same conditions but changing the concentration of $AgNO_3$ from 75 to 500 mM. Figure 3 (as well as Figure S3, Supporting Information, a low-magnification SEM image of Figure 3D) shows the SEM images of as-synthesized products. It was found that the AgNWs with high aspect ratios could be fabricated in this entire concentration range. Estimated from their SEM images, the yield of 1D products is at least 80 wt % at all different concentrations, and it increases to some extent with decreasing concentration (e.g., >85 wt % at a $AgNO_3$ concentration of 150 mM). Moreover, there exists an observable relation between the $AgNO_3$ concentration and the product dimension; that is, the average diameter becomes thicker and the distribution range of diameters becomes relatively larger with increasing concentration. From the manual counting result, the average diameter increases from ~100 to ~300 nm with the $AgNO_3$ concentration increasing from 75 to 500 mM. As indicated in Figure 3 and Figure S3 of the Supporting Information, a diameter over 200 nm is seldom found in the products synthesized below 150 mM, but a diameter over 250 nm

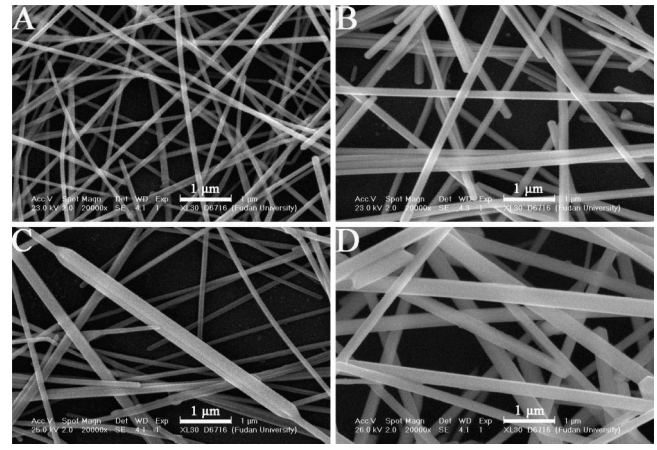

Figure 3. SEM images of products prepared through the SAP method at different concentrations of $AgNO_3$, (A) 75, (B) 150, (C) 250, and (D) 500 mM, while keeping the molar ratio between PVP and $AgNO_3$ at 1.5.

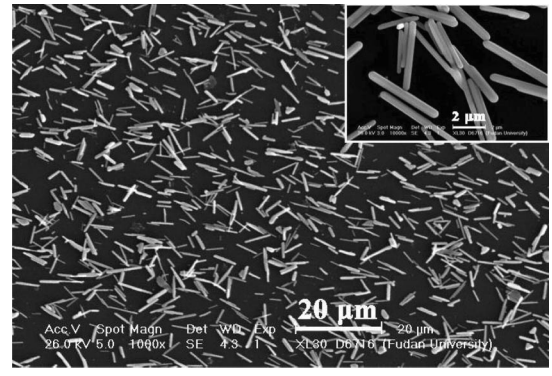

Figure 4. SEM images of products prepared from $AgNO_3$ (650 mM)/PVP (975 mM)/EG through the SAP method.

begins to appear in the 250 mM sample and becomes the majority in the 500 mM sample. In a word, the higher concentration results in the "fatter" product. This relation holds great promise for designing the dimension of AgNWs by changing the synthetic concentration. Interestingly, even if the concentration of $AgNO_3$ was further increased to 650 mM, 1D products were still obtained but with shorter lengths and thicker diameters (see Figure 4). This demonstrates that the SAP method is a high-efficiency means to obtain AgNWs.

Multidiameter Nanowires and Grooves on the Surfaces of AgNWs. Two interesting phenomena were also discovered during the high-concentration preparation of AgNWs. Some multidiameter nanowires (MDNWs) of silver can be observed in products prepared above 250 mM (see Figure 5A,B). These MDNWs indicate the existence of "fat-to-slim" and "slim-to-fat" transformations in one individual AgNW. Without any bend or break in the ridged structure along the MDNW (indicated by the arrow in Figure 5A), it implies a consistency of twin planes. This suggests that the MDNWs were formed originally in the synthetic process rather than end-to-end assembled[12] by several single wires. And also, the elongation of the re-entrant grooves on the surfaces of AgNWs have been found to be parallel to the twin planes (see Figure 5C,D). These re-entrant grooves were primarily found at the twin boundaries of a decahedron (the

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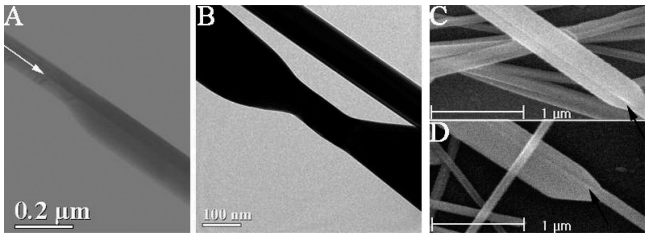

Figure 5. TEM image of a MDNW of silver with a (A) bowling-like and (B) dumbbell-like or Korean drumlike shape in the middle joint. (C and D) SEM images of AgNWs on which there are re-entrant grooves parallel to their central axis.

shape of multiply twinned particles, MTPs) and, also, were expected to rapidly grow out in the initial stage, because they provided highly favorable sites for atomic addition.[8] These phenomena have not been found in the process of low-concentration synthesis and are expected to provide more clues for the exact growth mechanism by which Ag seeds develop into 1D structures.

Discussion

The high-concentration synthesis of AgNWs has been achieved by introducing stainless steel into the polyol synthesis. And the diameter of AgNWs was adjustable by varying the synthetic concentration. Without the stainless steel, it was inclinable to form silver nanoparticles at relatively high concentrations. This indicates that stainless steel plays a critical role in the SAP method. To elucidate its effect in the SAP method, the mechanism for high-concentration polyol synthesis of silver nanostructures is discussed below.

Mechanism for the High-Concentration Preparation of AgNWs. According to the literature for conventional polyol synthesis,[13] the formation of silver nanostructures was started by the reduction of silver ions through reactions 1 and 2.

$$2HOCH_2CH_2OH \rightarrow 2CH_3CHO + 2H_2O \quad (1)$$

$$2AgNO_3 + 2CH_3CHO \rightarrow CH_3COOCCH_3 + 2Ag + 2HNO_3 \quad (2)$$

Once the concentration of Ag atoms had reached the supersaturation value, they would agglomerate to form Ag seeds fluctuating between single-crystal seeds and MTPs. The former (kinetically stable) would grow into nanoparticles, while the latter (thermodynamically stable) would grow into 1D nanostructures.[14,15] The thermodynamically favored MTPs were able to massively form and grow when the $AgNO_3$ concentration decreased to a sufficiently low level.[15a] According to this mechanism, MTPs and their resultant 1D products would be the predominant product only at a relatively low concentration of $AgNO_3$.

On the other hand, even at a low concentration of $AgNO_3$ (<27 mM), which was believed to be suitable for the polyol synthesis of AgNWs, Ag nanoparticles were still able to be obtained under the existence of small amounts of corrosive ions, such as Cl^- or Br^-.[16] This phenomenon was ascribed to MTPs with twin boundary defects having a stronger reactivity and susceptibility toward etching, while single-crystal seeds without defects were more stable in this environment and continued to grow.[16a,17] Therefore, for the sake of fabricating AgNWs, any etching of MTPs should be avoided in the stage of seed formation and rearrangement. However, it was noticed from reaction 2 as well as the experimental observations that HNO_3 was massively generated during the process, especially in the case of the high-concentration synthesis. Though some HNO_3 decomposed in the initial stage, some remained in the solution. This was a remarkable phenomenon worthy of note, considering the strong etching and corrosion ability of nitric acid. Actually, the restraint of MTP formation by nitric acidic etching has been reported through the additional introduction of a small amount of nitric acid (0.25 mM).[13] However, the selective etching of MTPs by the *in situ* generated nitric acid was likely neglected.

On the basis of the above arguments, the authors propose that the *in situ* generated nitric acid is a "poison" for the polyol synthesis of AgNWs, owning to its strong etching power. If it cannot be removed immediately, the etching ability of the mixture solution will dramatically increase with the progress of the reaction (reaction 2). When the concentration of HNO_3 reaches a sufficiently high level, most of the MTPs can be selectively eliminated before they grow into AgNWs, leaving only the single-crystal seeds to grow. However, in the SAP method, the addition of stainless steel pieces can facilitate the polyol synthesis of AgNWs in a high-concentration system through their corrosive reaction with nitric acid. The *in situ* generated nitric acid is partly consumed in the presence of stainless steel, resulting in the survival of MTPs for the growth of AgNWs. On the other hand, the stainless steel rarely has a replacement reaction with silver ions and iron due to its weaker reductive ability, hereby minimizing its additional influence on AgNW synthesis. Figure 6 schematically demonstrates the mechanism of polyol synthesis at high synthetic concentrations.

Effects of Air Flow and Reaction Temperature. It was also found that the introduction of bubbled air could improve the proportion of AgNWs in the resultant product (Figure 7). This phenomenon further validated the nitric acidic etching mechanism. The bubbled air could remove the resultant nitric oxides and thereby accelerated the reaction

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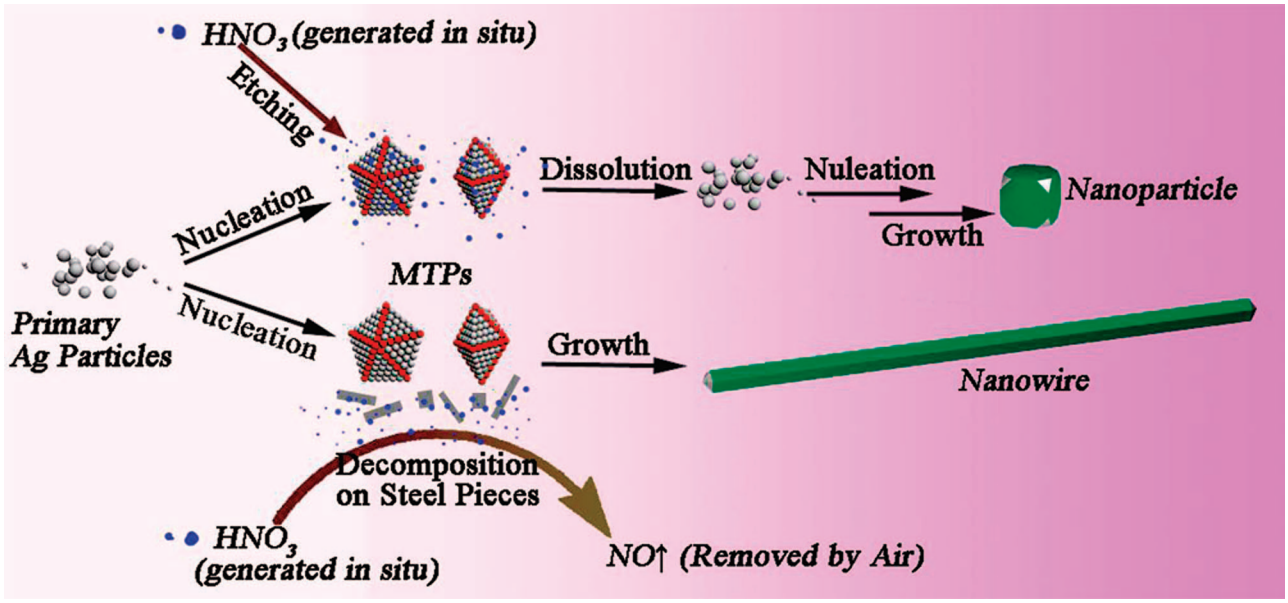

Figure 6. Scheme of the proposed mechanism for polyol synthesis at a relatively high synthetic concentration.

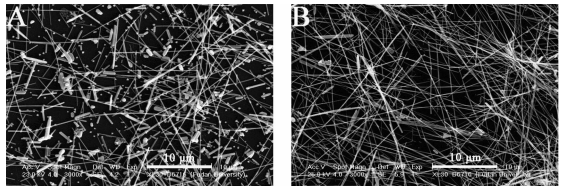

Figure 7. SEM images of products prepared from $AgNO_3$ (250 mM)/PVP (375 mM)/EG through the SAP method (A) without and (B) with bubbling air.

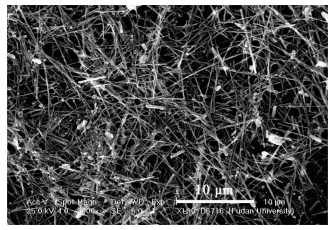

Figure 8. SEM images of products prepared at 140 °C throughout the entire process without the first 120 °C stage. Other conditions were the same as those indicated in Figure 7B.

between stainless steel and nitric acid, as well as the self-decomposition of nitric acid.

As concerning the reaction temperature, the SAP method was carried out at relatively milder temperatures. The first step of reflux at 120 °C was found to play an important role for the formation of AgNWs. When the reaction mixture was directly heated at 140 °C for 1 h (Figure 8), the products contained more irregular Ag particles. The lower temperature could slow down the reaction rate, providing a longer time available for the reaction between stainless steel and nitric acid. Meanwhile, the slow reaction rate was also beneficial for the nucleation of MTPs since their twin-crystal defects needed more time to form.[15a] On the contrary, overlow temperatures cannot provide enough energy for the activation of specific faces for the anisotropic growth of AgNWs.[6a]

Etching of MTPs by HNO_3/Halide Combinations in the Halide-Containing System. The existence of nitric acid is expected to additionally explain the difficulty of synthesizing AgNWs in halide-containing systems. It has been extensively reported that the addition of small amounts of halide salts (such as NaCl and NaBr) resulted in the preferential etching of twinned particles, leaving only the single-crystal particles to grow.[13,16] Xia et al. attributed it to the enhanced oxidation and dissolution of twinned particles by O_2/Cl^- or O_2/Br^-.[16] However, when considering the stronger corrosive ability of HNO_3/halide combinations[18] versus that of oxygen/halide pairs, the former may contribute more influence on the product morphology. The high reactivity of MTPs toward to the etching of HNO_3/halide combinations also leads to the selectively dissolution of them, so it is hard to form AgNWs in the halide-containing system.

Conclusion

In summary, the SAP method is considered as a good approach to the fabrication of AgNWs at high concentrations. It is proposed that *in situ* nitric acidic etching of MTPs is one of the most harmful factors for the polyol synthesis of AgNWs. By introducing stainless steel, the synthesis of AgNWs with high aspect ratios could be achieved, even at a $AgNO_3$ concentration of 500 mM. Meanwhile, the diameters of AgNWs could be adjusted in this method by changing the initial concentration of $AgNO_3$. This effective and facile technique for the mass production of AgNWs will give support for their promising commercial applications.

On the other hand, the mechanism of *in situ* nitric acidic etching presented here may have a significant impact on the development of wet chemical methods for the nanostructure synthesis of metals because corrosive acids are common byproducts generated in the synthetic process. Even though their amounts in the system are small, their strong corrosive power has the most profound influence on product morphol-

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ogy. In conjunction with the reported investigations,[13,16,19] it is expected that the intensity of etching can be controlled by adding various etching-enhanced or etching-restrained agents for the formation of seeds with specific nanostructures. This etching-controlled strategy will stimulate the synthesis research and business applications of silver and other metal nanostructures.

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Supporting Information Available: The optical photograph of the resultant reaction mixture, the EDX spectrum of the product, and the low-magnification SEM image of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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