Convenient, Rapid Synthesis of Ag Nanowires

Linfeng Gou, Mircea Chipara, and Jeffrey M. Zaleski*

Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington, Indiana 47405

Received January 17, 2007

The rapid, microwave-assisted aerobic synthesis of silver nanowires based on the polyol method is described. Benchtop dissolution of NaCl and $AgNO_3$ (ratio 1:6 to 1:3) in ethylene glycol and subsequent heating using microwave irradiation (300 W) in the presence of polyvinylpyrrolidone generates Ag nanowires in ∼80% yield in 3.5 min. Upon purification, microscopy (TEM, SEM) and powder X-ray diffraction reveal a uniform set of crystalline Ag nanowires with dimensions of 45 nm × 4−12 μm. Wire formation is highly dependent upon the microwave heating power, time, and $NaCl:AgNO_3$ ratio because of the rapid heating process and the presence of O_2 as an etching coreagent. Extended microwave heating causes the wires to fuse if in proximity or degrade to shorter wires presumably via the etching reaction. In the absence of O_2/Cl^-, the wires melt upon extended microwave heating (>4 min), suggesting that nanowire melting may contribute to the observed morphology under etching conditions. Compared to existing wet-chemical methods using traditional heating techniques, microwave irradiation not only rapidly heats, but dielectric heating of the growing wires also occurs, resulting in accelerated deposition of Ag^0 at the wire ends. Furthermore, this high yielding preparation does not require any external seed crystals, precursors, or mechanical stirring and is conducted under ambient O_2 conditions, leading to significant potential for the large-scale fabrication of Ag nanowires using this simple approach.

Introduction

One-dimensional (1D) metallic nanostructures have considerable potential in emerging technology arenas due to their unique electrical, optical, magnetic, and thermal properties and the potential applications in microelectronics, optoelectronic devices, and sensors.[1−13] Among the metals, silver nanowires have received considerable attention due to the high electrical and thermal conductivities of bulk silver, which is an important material in many fields. In addition, Ag nanowires have found interesting applications as optical polarizers,[14] photonic crystals,[15] and catalysts,[16] as well as in biomedical and chemical sensing via surface-enhanced Raman scattering (SERS)[7,17] and surface-enhanced fluorescence (SEF).[18]

Silver nanowires can be prepared within hard templates such as porous alumina membranes, carbon nanotubes, and block copolymers.[19−21] The use of templates ensures good control of the nanowire morphology. However, the diameter of nanowires is limited to the pore size of the template and the amount of product is limited to the ability and cost of fabricating templates. Alternatively, seeded and seedless wet-chemical methods have also been developed for the Ag nanowire synthesis.[22−27] It is well-known that the 1D nanowire structure is not the most favorable structure on the nanoscale. Therefore, to ensure growth in 1D, most wet chemical methods utilize a weak reducing agent, so that the reaction proceeds very slowly (1−10 h). However, because weak reducing agents are used, the reaction normally requires markedly elevated temperatures (>100 °C). Traditional oven

* Corresponding author. E-mail: zaleski@indiana.edu.

(1) Pascual, J. I.; Mendez, J.; Gomez-Herrero, J.; Baro, A. M.; Garcia, N.; Landman, U.; Luedtke, W. D.; Bogachek, E. N.; Cheng, H. P. *Science* **1995**, *267*, 1793−1795.
(2) Walter, E. C.; Ng, K.; Zach, M. P.; Penner, R. M.; Favier, F. *Microelectr. Eng.* **2002**, *61−62*, 555−561.
(3) Wu, Y.; Xiang, J.; Yang, C.; Lu, W.; Lieber, C. M. *Nature* **2004**, *430*, 704.
(4) Strevens, A. E.; Drury, A.; Lipson, S. M.; Kroell, M.; Blau, W. J.; Hoerhold, H. H. *Appl. Phys. Lett.* **2005**, *86*, 143503/1−143503/3.
(5) Murphy, C. J.; Sau, T. K.; Gole, A.; Orendorff, C. J. *MRS Bull.* **2005**, *30*, 349−355.
(6) Daniel, M.-C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346.
(7) Tao, A. R.; Yang, P. *J. Phys. Chem. B* **2005**, *109*, 15687−15690.
(8) Whitney, T. M.; Jiang, J. S.; Searson, P. C.; Chien, C. L. *Science* **1993**, *261*, 1316−1319.
(9) Ciraci, S.; Buldum, A.; Batra, I. P. *J. Phys.: Condens. Matter* **2001**, *13*, R537−R568.
(10) Wu, B.; Heidelberg, A.; Boland, J. J. *Nat. Mater.* **2005**, *4*, 525−529.
(11) Atashbar, M. Z.; Singamaneni, S. *Sens. Actuators, B* **2005**, *111−112*, 13−21.
(12) Kovtyukhova, N. I.; Mallouk, T. E. *Chem.−Eur. J.* **2002**, *8*, 4354−4363.
(13) Patolsky, F.; Lieber, C. M. *Mater. Today* **2005**, *8*, 20−28.
(14) Pang, Y. T.; Meng, G. W.; Fang, Q.; Zhang, L. D. *Nanotechnology* **2003**, *14*, 20−24.
(15) Hu, X.; Chan, C. T. *Appl. Phys. Lett.* **2004**, *85*, 1520−1522.
(16) Chimentao, R. J.; Kirm, I.; Medina, F.; Rodriguez, X.; Cesteros, Y.; Salagre, P.; Sueiras, J. E. *Chem. Commun.* **2004**, 846−847.

(17) Jeong, D. H.; Zhang, Y. X.; Moskovits, M. *J. Phys. Chem. B* **2004**, *108*, 12724−12728.
(18) Aslan, K.; Lakowicz, J. R.; Geddes, C. D. *Anal. Bioanal. Chem.* **2005**, *382*, 926−933.
(19) Govindaraj, A.; Satishkumar, B. C.; Nath, M.; Rao, C. N. R. *Chem. Mater.* **2000**, *12*, 202−205.
(20) Zhang, D.; Qi, L.; Ma, J.; Cheng, H. *Chem. Mater.* **2001**, *13*, 2753−2755.
(21) Zong, R.-L.; Zhou, J.; Li, Q.; Du, B.; Li, B.; Fu, M.; Qi, X.-W.; Li, L.-T.; Buddhudu, S. *J. Phys. Chem. B* **2004**, *108*, 16713−16716.
(22) Caswell, K. K.; Bender, C. M.; Murphy, C. J. *Nano Lett.* **2003**, *3*, 667−669.
(23) Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, *14*, 80−82.
(24) Sun, Y.; Xia, Y. *Adv. Mater.* **2002**, *14*, 833−837.
(25) Sun, Y.; Yin, Y.; Mayers, B. T.; Herricks, T.; Xia, Y. *Chem. Mater.* **2002**, *14*, 4736−4745.
(26) Wang, Z.; Liu, J.; Chen, X.; Wan, J.; Qian, Y. *Chem.−Eur. J.* **2005**, *11*, 160−163.
(27) Jiang, P.; Li, S.-Y.; Xie, S.-S.; Gao, Y.; Song, L. *Chem.−Eur. J.* **2004**, *10*, 4817−4821.

Gou et al.

heating is fundamentally inefficient as the heat capacity of the reaction chamber and solvent need to be satisfied to reach the required temperature to promote reactivity. In contrast, thermal activation by microwave heating is considerably more efficient, generating rapid temperature increases and even local heating that may favor kinetically competent, nonequilibrium chemical processes.

Microwave irradiation has been used to accelerate the preparation of inorganic nanoparticles,[28−35] as well as 1D nanostructures such as nanotubes (carbon, CdS, TiO_2), nanorods, and nanowires (Ag, Au, ZnS, ZnSe, Se, Bi).[34,36−45] For 1D Ag nanostructures specifically, Zhu et al. reported the microwave-mediated synthesis of Ag nanowires by reducing Ag_2O in 1,2-ethanedithiol (10 min, 80−140 °C), whereas in ethylene glycol, the reaction produces spherical particles.[46] Using H_2PtCl_6 as a source of Pt seeds,[47,48] Tsuji's research group successfully achieved the microwave synthesis of Ag nanorods and wires in ethylene glycol in 8 min. In a movement to aqueous solution, Liu et al. and Yu et al. reported the microwave-assisted formation of Ag nanorods and Ag/C nanocables within 10 and 20 min, respectively. In both cases, high-pressure vessels were required, as reaction temperatures exceeded 100 °C.[49,50]

As illustrated by these studies, one obvious advantage of combining microwave irradiation with solution-phase, hydrothermal/solvothermal synthetic approaches is the marked decrease in reaction time from more than 1 h in traditional wet-chemical syntheses to less than 20 min using microwave activation. This advantage, however, can come at the cost of procedural simplicity as special microwave apparatuses,

nanocrystal seeding strategies, or pressure-safe reaction vessels compromise the straightforwardness of the microwave-assisted synthetic method.

Herein, we demonstrate the rapid, aerobic preparation of uniform Ag nanowires by introducing microwave irradiation and chemical modifications to the polyol synthesis method developed by Xia et al. [24,25] We choose the polyol synthesis as a template because of its simplicity and the fact that the reaction parameters and mechanism have been well-studied. Moreover, the polyol synthesis recently has been employed in the preparation of many other metal and metal oxide nanoparticles.[51,52] Our results show that modification of solution conditions and incorporation of microwave irradiation can reduce the reaction time required to form extended, 1D Ag nanostructures in high uniformity to ∼3.5 min. The modified procedure requires only simple reagents and equipment, can be carried out under aerobic conditions, and does not require seeding protocols or ultra-fine control over the temperature and pressure. Finally, the approach leads to nanomaterial in high yield, making it very cost-effective and potentially competitive for the large-scale production of uniform Ag nanowires.

Experimental Section

All chemicals ($AgNO_3$, NaCl, ethylene glycol (EG), and polyvinylpyrrolidone (PVP, MW ∼55000)) were obtained from Aldrich and used as received. A commercially available microwave operating at powers of 100−1000 W was used as the heating source in this study.

In a typical experiment, 9.0 mg of $AgNO_3$ and 110 mg of PVP were dissolved consecutively in 20 mL of EG in a flask, leading to final solution concentrations of 0.026 and 0.05 M, respectively. To parallel solutions, varying amounts of NaCl were added. The solutions were sonicated to speed the dissolution of the solid powders. Immediately upon addition of NaCl, the entire solution becomes an opaque, opal color due to the formation of AgCl colloidal particles. The solutions were then transferred to the microwave oven operating at 2.45 GHz and heated with different heating cycles from 0.5 to 5 min. To monitor the growth process of the nanostructures, we took samples and measured the solution temperature after each 30s heating step. Upon completion of the reaction, solutions were allowed to cool in air for 2 min. The final product was washed first with acetone to remove ethylene glycol and excess surfactant PVP and then multiple times with deionized water, following the wash−centrifuge−redisperse purification cycle to remove small, quas-spherical Ag nanoparticles. After removing EG and PVP, we characterized the samples using a JEOL 1010 transmission electron microscope (TEM) at 80 kV, a LEO 1430 scanning electron microscope (SEM) at 15 kV, and powder X-ray diffraction (XRD) on a Scintag diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.541874$ Å) at a scanning rate of 0.02° s^{-1} in the 2θ range from 20 to 80°.

Results and Discussion

Solutions containing 0.026 M $AgNO_3$ and 0.050 M PVP in 20 mL of EG (reductant) were heated aerobically in a

(28) Chen, W. X.; Lee, J. Y.; Liu, Z. *Chem. Commun.* **2002**, 2588−2589.
(29) Komarneni, S.; Li, D.; Newalkar, B.; Katsuki, H.; Bhalla, A. S. *Langmuir* **2002**, *18*, 5959−5962.
(30) Tsuji, M.; Hashimoto, M.; Tsuji, T. *Chem. Lett.* **2002**, 1232−1233.
(31) Chen, D.; Tang, K.; Shen, G.; Sheng, J.; Fang, Z.; Liu, X.; Zheng, H.; Qian, Y. *Mater. Chem. Phys.* **2003**, *82*, 206−209.
(32) Zhang, Y.; Qiao, Z.-P.; Chen, X.-M. *J. Mater. Chem.* **2002**, *12*, 2747−2748.
(33) Harpeness, R.; Gedanken, A.; Weiss, A. M.; Slifkin, M. A. *J. Mater. Chem.* **2003**, *13*, 2603−2606.
(34) Hong, E. H.; Lee, K.-h.; Oh, S. H.; Park, C.-g. *Adv. Funct. Mater.* **2003**, *13*, 961−966.
(35) Mendez, U. O.; Kharissova, O. V.; Rodriguez, M. *Rev. Adv. Mater. Sci.* **2003**, *5*, 398−402.
(36) Shao, M.; Xu, F.; Peng, Y.; Wu, J.; Li, Q.; Zhang, S.; Qian, Y. *New J. Chem.* **2002**, *26*, 1440−1442.
(37) Liu, F.-K.; Chang, Y.-C.; Ko, F.-H.; Chu, T.-C. *Mater. Lett.* **2003**, *58*, 373−377.
(38) Lu, Q.; Gao, F.; Komarneni, S. *J. Mater. Res.* **2004**, *19*, 1649−1655.
(39) Panda, A. B.; Glaspell, G.; El-Shall, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 2790−2791.
(40) Liu, X.; Tian, B.; Yu, C.; Tu, B.; Zhao, D. *Chem. Lett.* **2004**, *33*, 522−523.
(41) Tsuji, M.; Hashimoto, M.; Nishizawa, Y.; Tsuji, T. *Mater. Lett.* **2004**, *58*, 2326−2330.
(42) Zhu, Y.-j.; Hu, X.-l. *Chem. Lett.* **2003**, *32*, 1140−1141.
(43) Zhu, Y.-J.; Hu, X.-L. *Chem. Lett.* **2003**, *32*, 732−733.
(44) Wang, Y.-a.; Yang, J.; Zhang, J.; Liu, H.; Zhang, Z. *Chem. Lett.* **2005**, *34*, 1168−1169.
(45) Zhou, B.; Ren, T.; Zhu, J.-J. *Int. J. Mod. Phys. B* **2005**, *19*, 2829−2834.
(46) Zhu, Y.-J.; Hu, X.-L. *Mater. Lett.* **2004**, *58*, 1517−1519.
(47) Tsuji, M.; Hashimoto, M.; Nishizawa, Y.; Kubokawa, M.; Tsuji, T. *Chem.−Eur. J.* **2005**, *11*, 440−452.
(48) Tsuji, M.; Nishizawa, Y.; Hashimoto, M.; Tsuji, T. *Chem. Lett.* **2004**, *33*, 370−371.
(49) Liu, F.-K.; Huang, P.-W.; Chang, Y.-C.; Ko, F.-H.; Chu, T.-C. *J. Mater. Res.* **2004**, *19*, 469−473.
(50) Yu, J. C.; Hu, X.; Li, Q.; Zhang, L. *Chem. Commun.* **2005**, 2704−2706.

(51) Feldmann, C.; Jungk, H.-O. *Angew. Chem., Int. Ed.* **2001**, *40*, 359−362.
(52) Mu, Y.; Liang, H.; Hu, J.; Jiang, L.; Wan, L. *J. Phys. Chem. B* **2005**, *109*, 22212−22216.
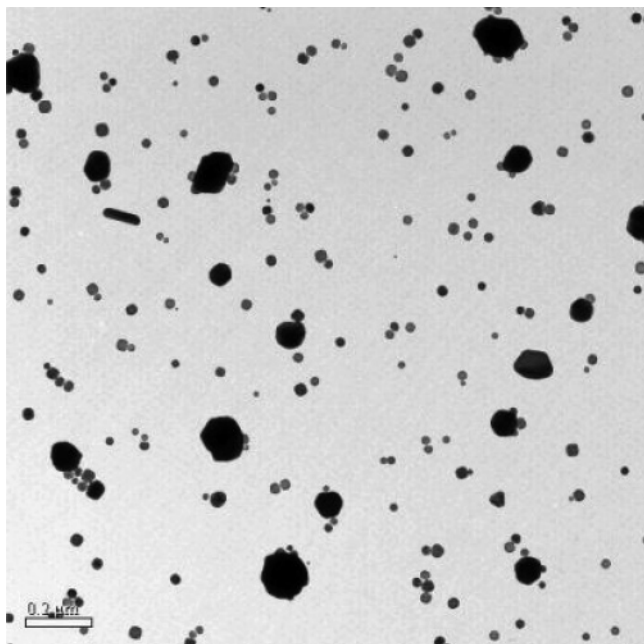
Figure 1. Silver nanocubes/nanoparticles formed at a NaCl:AgNO$_3$ ratio of <1:6. Scale bar: 0.2 μm.

standard microwave oven at 300 W for 3.5 min. In the absence of NaCl, or in low concentrations relative to AgNO$_3$ (≪1:6), the main nanostructured products of the reaction are spherical, quasispherical, and cubic Ag nanoparticles (Figure 1). These basic morphological components are retained even as heating conditions such as power (100-100W) and time (1−5 min). Analogous nanostructured products deriving from conventional anaerobic heating at 140−180 °C for >1 h have been previously reported.[26,53]

Increase in the NaCl concentration relative to AgNO$_3$ (1: 6) results in marked changes in the nanostructure speciation in solution, highlighted by the formation of Ag nanowires. Microwave heating of AgCl/EG/PVP solutions at 100−1000 W with a 1:6 NaCl:AgNO$_3$ ratio generates a myriad of solution colors as a function of power and heating time (Table 1, Figure 2), indicative of the evolution of various nanostructure products. At low heating powers (e.g., 100−200 W) and reaction times of 4−6 min, the solution turns from an opaque opal color characteristic of colloidal AgCl, first to yellow, indicative of the formation of irregular/ quasispherical particles (cf. panels a and b of Figure 2), and then to gray, which is commensurate with the initial formation of nanowire products as determined by TEM analysis. An increase in the heating power to 300 W with a concomitant decrease in aerobic reaction time to 3−4 min leads to formation of orange-red solutions (Figure 2c−e) that turn brown after 4 min (panels f and g of Figure 2). As the aerobic heating time is increased in 30 s intervals, a distinct increase in the composition of nanorods and longer, uniform nanowires is observed, peaking at ∼3.5 min. Heating at higher microwave powers or longer reaction times leads to degradation of the nanowires to a variable mixture of quasispherical and cubic Ag nanostructures. Overheating by

microwave irradiation can fuse (see the Supporting Information) or possibly even melt (vide infra) the nanowires, which gradually break down to smaller rods. Decreasing the salt concentration induces the formation of many nucleation sites for spherical nanoparticles, resulting in low nanowire yield. Increasing the salt concentration to 1:3 requires an increase in reaction time to ∼5 min. A further increase in salt concentration slows the reaction considerably and lengthens the aerobic heating time beyond 5 min, after which time the EG solvent/reductant begins to vaporize. Thus, aerobic heating of a EG/PVP solution 1:6−1:3 NaCl:AgNO$_3$ molar ratio at 300 W for ∼3.5 min is a highly favorable reaction condition for rapid, aerobic synthesis of Ag nanowires.

The crude reaction solution contains small amounts of nanoparticles that can be removed by acetone and subsequent water dispersion and centrifugation. Using this method, a purity of the final nanowires greater than 95% can be realized, as shown in both the TEM (Figure 3) and SEM images (Figure 4) obtained on at different magnifications on the micrometer and nanometer scales. In these images, very few nonwire Ag nanostructures are observed ,even over a very broad visualization range. The enlarged TEM image (Figure 3b) reveals that the nanowires are quite uniform in their dimensions, with an average diameter of 45.2 ± 4.2 nm and a length from 4 to 12 μm. The edges of the nanowires exhibit a pentagonal crystalline structure (inset, Figure 3b) similar to that observed for the synthesis of Ag nanowires by the polyol method[24] and indicative of seeds deriving from twinned bicrystalline particles of decahedral shape. The powder X-ray diffraction pattern of the nanowire samples (Figure 5) reveals prominent Bragg diffraction that can be indexed to microcrystalline Ag^0 and not Ag(I) species such as AgCl and Ag$_2$O. Prominent diffraction peaks from the {111} (nanowire ends) and {200} (nanowire body) faces, as well as the remaining features, are identical to those in diffraction patterns observed for other Ag nanowires with different length and width dimensions.[25,27]

The polyol synthesis developed by Fiévet[54] and extended by Xia[24,25,55] is an outstanding method for controlling nanoparticle shape selectivity and nanowire growth in solution. The productivity of the reaction relies on heating of a Ag$^+$ source in solution with a reductant (e.g., EG, solvent) to above 100 °C, where reduction to Ag^0 can occur. These conditions produce spherical/quasispherical Ag nanoparticles but no nanowires. Heating to >145 °C for ∼1 h with external addition[55] or in situ development of a seed[24] is required for nanowire growth to propagate in a single dimension. The kinetics of single-crystal formation, thermodynamic stability of specific crystalline structures,[56] and the topology of these seeds are all critical factors in the dynamic solution equilibrium that controls nanowire growth.

Our results show that microwave heating at 300 W for 2 min raises the solution temperature to ∼170 °C, activating

(53) Sun, Y.; Mayers, B.; Herricks, T.; Xia, Y. *Nano Lett.* **2003**, *3*, 955−960.

(54) Fievet, F.; Lagier, J. P.; Figlarz, M. *MRS Bull.* **1989**, *14*, 29−34.
(55) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, *2*, 165−168.
(56) Wiley, B.; Herricks, T.; Sun, Y.; Xia, Y. *Nano Lett.* **2004**, *4*, 1733−1739.
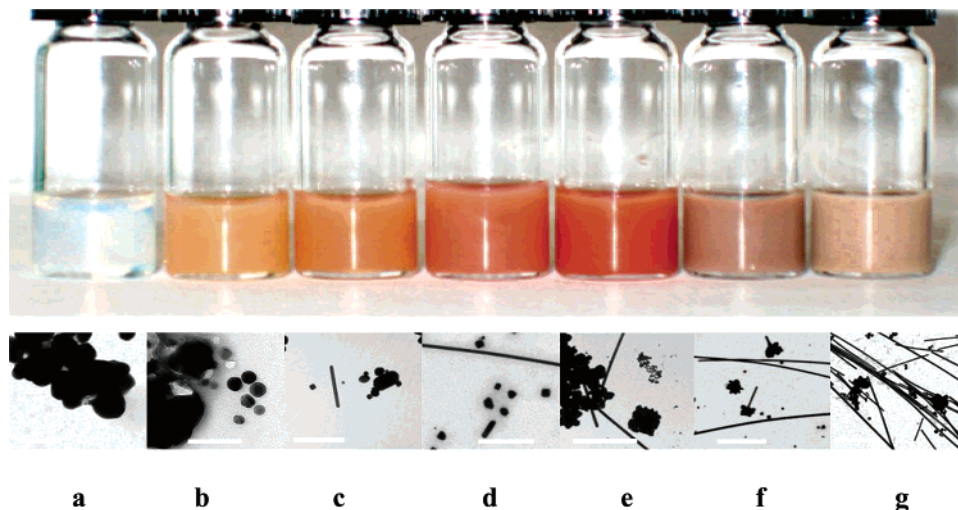
Figure 2. Ag nanostructures formed at different heating times from 30 to 210 s (left to right) at a microwave power of 300 W and a 1:6 NaCl:AgNO$_3$ ratio. The photographs (a–g) represent the as-synthesized products at 30, 60, 90, 120, 150, 180, and 210 s, respectively. The corresponding enhanced TEM images show the nanostructure composition during each 30 s heating cycle. The data reveal the evolution from large AgCl aggregates to small Ag nanoparticles with AgCl aggregates, the decrease of AgCl aggregates and the beginning of short nanorod formation, short nanorod growth into longer wires, and finally, generation of uniform nanowires (see the Supporting Information for full TEM images). Scale bars: (a) 200 nm, (b) 100 nm, (c) 500 nm, (d) 500 nm, (e) 1 μm, (f) 1 μm, (g) 1 μm.

Table 1. Microwave Reaction Conditions for Formation of Ag Nanomaterial Products

heating cycles	solution color[a]	product distribution
100 W × 6 min	yellow	irregular/quasispherical particles
200 W × 6 min	gray-brown to gray-white	nanowires + quasispherical/cubic particles
300 W × ≤3 min	orange to red-brown	some nanowires + quasispherical/cubic particles
300 W × 3.5 min	gray-brown	mainly nanowires + quasispherical/cubic particles
300 W × ≥ 4 min	brown	nanowires /rods + quasispherical/cubic particles
400 W × 3 min	gray-brown	mainly nanowires + quasispherical/cubic particles
300 W × 2 min + 400 W × 2 min	brown	shorter nanowires /rods + quasi-spherical/cubic particles + dendrite-like aggregates
1000 W × 1 min	red-brown	shorter nanorods + quasispherical/cubic particles

[a] Solutions contain a 1:6 NaCl:AgNO$_3$ ratio.

EG as a sacrificial reductant of Ag$^+$ according to the mechanism originally proposed by Fiévet[54]

$$CH_2OH\text{-}CH_2OH \rightarrow CH_3CHO + H_2O$$

$$2Ag^+ + 2CH_3CHO \rightarrow 2Ag^0 + CH_3COCOCH_3 + 2H^+$$
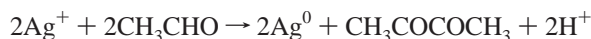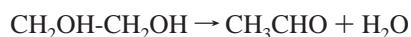
Continuous heating will raise the temperature an additional ~30 °C as the solution approaches the boiling point of the solvent. These conditions permit the general formation of Ag nanostructured products as sufficient thermal energy exists to initiate in situ reduction and seed formation. At higher microwave power, the solution temperature is raised so quickly that the O$_2$/Cl$^-$ etching process that controls the equilibrium by promoting seed dissolution (vide infra) is outpaced by the rate of seed formation, and only nanoparticles or small nanorods are formed.

Although the efficiency of microwave heating explains the rapidity of Ag nanostructure formation, it does not explain, a priori, the formation of Ag nanowires. As mentioned above, growth of 1D nanostructures usually requires slow reaction conditions to reduce the number of nucleation sites formed or equilibrium dissolution of these nucleation sites to promote site-specific 1D growth. Because it is well-known that PVP binds preferentially with the {100} facet of Ag crystal and

guides the growth in 1D along the {111} face,[57] this seed growth/dissolution equilibrium is dependent on two remaining factors. The first is Cl$^-$ reaction with Ag$^+$ to generate colloidal AgCl, which decreases the concentration of free Ag$^+$ ions in solution by acting as a buffer reaction. According to the Nernst equation, the decrease in Ag$^+$ concentration will cause a cathodic shift of the Ag$^{+/0}$ couple that will reduce the rate of formation of Ag^0 in solution.[58] Second, in the presence of ambient O$_2$, oxidative dissolution of the nanowires is aided by elevated concentrations of Cl$^-$ (i.e., etching).[53] Therefore, although rapid heating causes the formation of many nucleation sites simultaneously, the presence of O$_2$ and moderate Cl$^-$ concentrations serves to redissolve many of these sites, promoting growth of Ag nanowires in 1D. This dynamic equilibrium (Scheme 1) is in concert with the need for a 1:6 to 1:3 NaCl:AgNO$_3$ mole ratio for optimum nanowire growth. If [Cl$^-$] is too low, the conversion of Ag$^+$ to Ag^0 will be more rapid than the dissolution rate, thus promoting the formation of more quasispherical particles. If [Cl$^-$] is too high, the equilibrium for AgCl colloid formation increases, concomitant with an increase in the dissolution rate of the *in situ* seed, resulting in the need for increased reaction temperature to promote the cathodically shifted

(57) Aroca, R. F.; Goulet, P. J. G.; Dos Santos, D. S., Jr.; Alvarez-Puebla, R. A.; Oliveira, O. N., Jr. *Anal. Chem.* **2005**, *77*, 378–382.
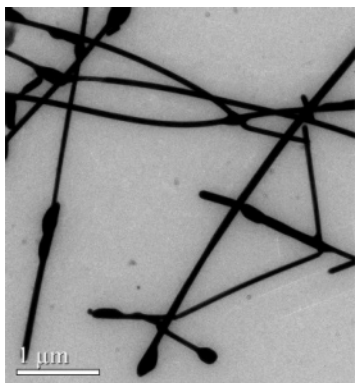(58) Yu, D.; Yam, V. W.-W. *J. Phys. Chem. B* **2005**, *109*, 5497–5503.

Figure 3. (a) TEM image of purified Ag nanowires with length ranging from 4 to 12 μm. Scale bar: 1 μm. (b) Enlarged TEM image of purified Ag nanowires illustrates the uniformity of the wires and an average width of ~45 nm. Scale bar: 200 nm. The inset shows the tip of one Ag nanowire exhibiting a pentagonal crystalline structure. Scale bar in the inset: 50 nm.

Figure 4. SEM image of Ag nanowires. Very few small particles are present, indicating the high purity of the material following the separation process.

reduction of Ag^+ to Ag^0. Finally, overheating causes the nanowire structures to fuse if in immediate proximity or breakdown to form nanoclusters and quasispheres presumably by elevated temperature etching.

Figure 5. Powder X-ray diffraction of Ag nanowires with diffraction peaks indexed to the crystalline Ag^0 nanowires. The (111) face corresponds to the ends of the nanowires.

Scheme 1. Proposed Mechanism for the Formation of Ag Nanowires[a]

   [a] NaCl induces the buffer reaction, which decreases the Ag^+ concentration by forming AgCl and impedes the conversion of Ag^+ to Ag^0; the presence of Cl^- results in the re-dissolution of most Ag^0 nuclei in air. By slowing the Ag^+/Ag^0 conversion and controlling the amount of Ag^0 nuclei, the buffer effect makes a controlled 1D growth possible.

With the rapid, microwave-assisted formation of Ag nanowires clear, the role of the excitation source remains to be considered. Because conventional thermal heating under our conditions for ~1 h at 170 °C can indeed begin to produce nanowire structures and preheating to ~170 °C using microwaves can reduce this time only to ~30 min, we questioned why the microwave reaction was so facile at the same solution temperature. One possibility is that the solvent is superheated, leading to elevated reaction temperatures, as Tsuji. et al. suggested.[47] Careful monitoring of the reaction temperature suggests that this is not the case, as the solution remains at about 170 °C up to 3.5 min. The other possibility is that the 2.45 GHz traveling microwave can accelerate nanowire growth by directly interacting with the growing wires as it does with metallic powders.[59] Bulk metals are well-known to reflect microwaves; however, in conducting materials that have very thin sections, the conducting electrons can be polarized by the oscillating microwave field, leading to charge flow, dielectric heating, and arc formation.[59] Because Ag nanowires are conducting,[55] superheating may result from field-induced electron polarization and charge localization. Indeed, when isolated Ag nanowires are placed inside a pyrex vial and heated at 300 W for 10 s, the material

(59) Whittaker, A. G.; Mingos, D. M. P. *Dalton Trans.* **2000**, 1521−1526.

Figure 6. TEM image of the structural change of purified Ag nanowires (redispersed in EG) upon microwave heating at 300 W for 5 min.

shows visible arcing and the pyrex container softens from the heat collected and dissipated by the nanowires, confirming the existence of charge flow and resistive heating. In EG solution, the heat generated by oscillation of the conducting electrons can be rapidly transferred to the surrounding media, generating the observation of a uniform reaction temperature.

Nanowire dielectric superheating also explains why Ag nanowires fuse and melt upon extended microwave exposure, a fact that cannot be reproduced by conventional heating at 180 °C for 30 min. Dispersion of pure Ag nanowires in 20 mL EG and subsequent microwave exposure (300 W, 4.5 min) induces bulb formation (Figure 6) deriving from melting of the nanowire structures in the absence of etching reagents (O_2/Cl^-). This observation further supports nanowire superheating during the growth phase and may contribute to the fused structures produced upon extended thermolysis (Scheme 1). It is noteworthy that although the microwave-induced superheating of silver nanowires is discussed here in a unique context, close analogs such as the thermal degradation of carbon nanotubes under electric stress have been previously reported.[60]

Microwave heating may also promote nanowire growth by a local "hot spot" effect at the wire ends. In support of this assertion, Schatz has evaluated the polarizability of noble metal truncated tetrahedral nanoparticles upon excitation of the plasmon resonance of the material and has shown that this leads to greater than 2 orders of magnitude increase in the local electric field at the vertices.[61] Because the ends of the nanowires are evolving sites with sharp defects, these positions may reach even higher temperatures than the wire midsection and accumulate charge due to polarization by the microwave field. The elevated temperature and charge localization may further designate the wire ends as preferential sites for deposition of Ag^0, with PVP already selectively protecting the longitudinal axis of the nanowire. Combined, these observations support the conclusion that elevated nanowire temperatures are contributing to the rapidity of the microwave reaction, at the same time explaining why higher concentrations of etching reagents (Cl^-/O_2) are tolerated and assist in the 1D growth phase.

Conclusion

In conclusion, the aerobic, microwave-assisted polyol synthesis of Ag nanowires results in the facile generation of uniform and high-purity (>95% after isolation) structures with average dimensions of 45 nm × 4−12 μm. Compared to existing wet chemical methods using traditional heating techniques, microwave irradiation generates a more rapid reaction due to interaction of the microwave field with the growing wire, leading to a nonequilibrium route to more uniform Ag nanostructure formation in solution. Furthermore, the preparation does not require any external seed crystals, precursors, or mechanical stirring and is conducted under ambient O_2 conditions, leading to significant potential for the large-scale fabrication of Ag nanowires using this approach. Under optimum conditions, this protocol can lead to gram-scale production within 30 min. Finally, the conceptual development of selective microwave heating may lead to the replacement of conventional heating in many hydrothermal and solvothermal reactions, reducing reaction times for nanostructure synthesis.

Supporting Information Available: Various TEM images of the as-synthesized products. This material is available free of charge via the Internet at http://pubs.acs.org.

CM070160A

(60) Kuroda, M. A.; Cangellaris, A.; Leburton, J.-P. *Phys. Rev. Lett.* **2005**, 95, 266803/1−266803/4.

(61) Schatz, G. C. *Theochem* **2001**, *573*, 73−80.